

# AN ELEMENTARY STUDY OF CHEMISTRY

W. L. NELSON AND HENDERSON

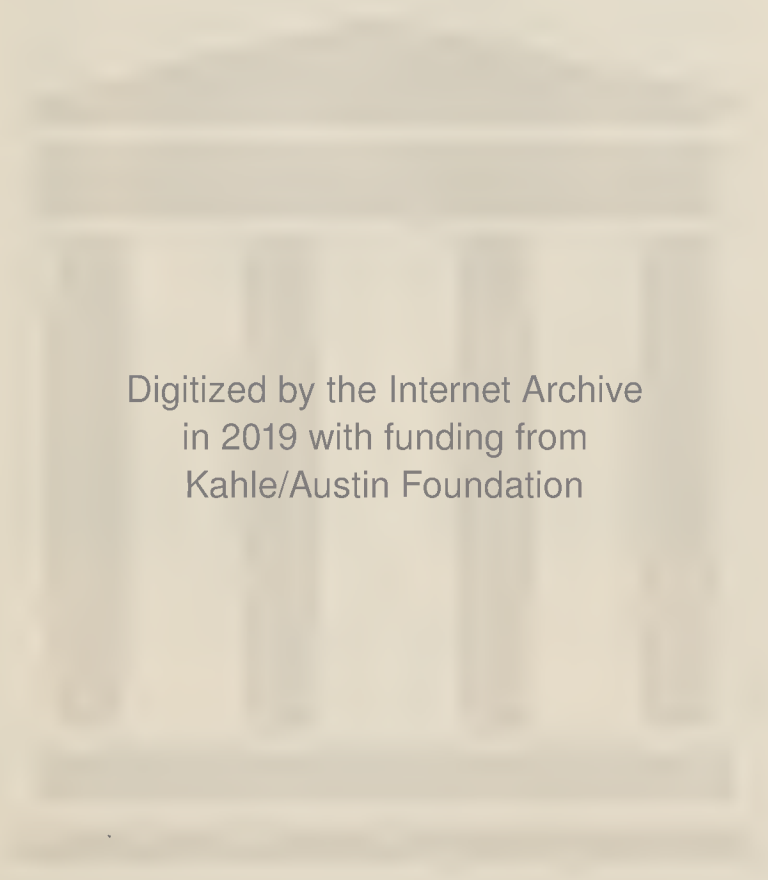


*W. R. Fleming.*









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ANTOINE LAURENT LAVOISIER,  
 FERMIER GÉNÉRAL NÉ A PARIS LE 16 AOUT 1743.  
*Jugé le 16 floréal l'an 2.*

ANTOINE LAURENT LAVOISIER (1743-1794)

Famous for his care in quantitative experiments, for demonstrating the true nature of combustion, for introducing system into the naming and grouping of chemical substances. Executed (1794) during the French Revolution because of his connection with the government. This picture is taken from a French engraving of 1799. The panel represents Lavoisier as he is being arrested in his laboratory by the Revolutionary Committee

# AN ELEMENTARY STUDY OF CHEMISTRY

INTRODUCTORY COLLEGE COURSE

BY

WILLIAM McPHERSON

AND

WILLIAM EDWARDS HENDERSON



GINN AND COMPANY

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## PREFACE TO THE THIRD EDITION

The past twenty years have witnessed a remarkable development in chemistry as a science and a great improvement in the method of its presentation to the beginning student. An especial interest was directed to chemistry during the World War because the public mind was impressed as never before by the dependence of our economic and social life upon the labors of the chemist, as well as by the remarkable achievements of organized chemical research directed to the solution of the many emergency problems of the time. Indeed, an earlier ignorance of what a chemist does was replaced by an almost unreasoning belief in impossible accomplishments. A great impetus was given to the interest of young people in this fundamental science, as well as to its importance in the minds of industrial leaders, and the reaction upon the progress of the science has been wholly beneficial.

Teachers of chemistry have responded with enthusiasm to this extended interest in chemistry by broadened preparation for their work and by demanding better textbooks for their use. In response to their demand a considerable number of excellent textbooks have appeared, and it is questionable whether any other science is so well provided with books suited to the beginner as is chemistry.

The present revision represents the best efforts of the authors to contribute their share to this higher requirement. With a number of minor modifications the general plan of presentation adopted in former editions has been retained, since experience and observation have seemed to show that a marked deviation from what has become a more or less standard plan

is not in general attended with success. Aside from the general scheme of presentation and the order in which topics are introduced, the merits of a textbook in chemistry lie chiefly in fidelity to most recent knowledge, a happy balance between theory and descriptive fact, the selection of illustrative material from those processes which have to do most intimately with everyday life and interesting industrial progress, and a simplicity of statement that is free from ambiguity, easy of understanding, and cast in at least a reasonably good model of English style. To this should be added an attention to the pictorial illustrations that enlists the best workmanship of the illustrator, renders the descriptive text really clearer instead of more obscure, creates interest, and adds a human quality to the science. To all these demands the authors have given their most faithful attention, and the greatest reward will be the knowledge that teachers are finding the book a helpful one in the initiation of youth to the attractions of chemical science.

The relation of the elementary textbook to industrial problems requires special comment to set forth clearly the views of the authors. They believe that the science loses much in interest if free reference to its applications in the industries is omitted, and that much practical knowledge is gained as a by-product by abundant comment on the way in which scientific facts become the foundation of industrial processes. They believe also that the author of a textbook should be at pains to have his statements regarding industrial practice conform to present usage as far as possible. They believe with equal conviction that an understanding of chemical industry is not the chief object in an elementary course; that industrial methods and processes should at all times constitute an illustration of the way in which the facts and theories of a science become the basis of an industry. They are convinced that *the real test of the success of an elementary course in chemistry must be found in the extent to which the pupil has been trained to grasp the fundamental facts and theories of the science and has learned*



*to reason correctly in chemical relations*, rather than in his knowledge of constantly changing industrial processes.

This new edition has been completely rewritten, and it is hoped that it will not disappoint those who have used it in the past, and that it will commend itself to new friends in the future. In preparing the cuts and securing information on industrial progress the authors have incurred a great weight of obligation to many individuals and commercial companies. It is impossible to mention all of these by name, but the authors desire to make special acknowledgment to the following: the Libbey-Owens Sheet Glass Company, the Lowe Brothers Paint Company, the Goodrich Rubber Company, the Warner Chemical Company, the Eastman Kodak Company, the Carnegie Museum, and the American Rolling Mills Company.

We wish also to acknowledge our very great indebtedness to many teachers for their suggestions. Especially are we indebted to the ripe experience and mature judgment of our colleagues, Mr. William Lloyd Evans, Mr. Dana J. Demorest, Mr. William J. McCaughey, Mr. Edward Mack, Jr., and especially Mr. Cloyd D. Looker, who read all the proof with great care and made many valuable suggestions.

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# AN ELEMENTARY STUDY OF CHEMISTRY

## CHAPTER I

### CHEMISTRY AND THE WORK OF THE CHEMIST

**Introduction.** As we proceed with the study of chemistry we shall find that the subjects with which we are most concerned are those which have to do (1) with **matter** and (2) with **energy**. It is difficult to frame a simple and accurate definition of these two terms. Later we shall consider both of them more in detail, but for the present we may regard matter as *anything which has mass*, for this is by far the most fundamental characteristic of matter. Energy, on the other hand, may be regarded as *the ability to do work*. Thus, a lump of coal is matter, for it possesses mass. It is equally clear that it possesses energy, for by means of it work can be performed, as when a heavily laden train is moved by using coal for fuel in the engine.

**Changes in matter.** Even the most superficial observer notices that matter is constantly undergoing change. In some cases this change takes place so rapidly that it is easily discernible. Thus, a pane of glass may be broken into pieces, or a lump of coal may be burned to ashes. Very often the change is not so rapid, but just as certainly occurs. For example, iron, exposed to moist air, slowly changes into the red product which we call iron rust. Rocks gradually disintegrate through the action of air, wind, and water, and form soil. The food that we eat is changed into muscle and bone,

and sooner or later the matter of all living organisms decays, passing into other forms. Everywhere in nature such changes are constantly taking place in almost every object within our observation.

**Physical changes and chemical changes.** If we examine with care the various changes which matter undergoes, it will become evident that they may be divided broadly into two classes. In the one class, typified by such changes as the breaking of glass or by the powdering of a lump of coal, the form or shape of the matter alone is changed, but its real nature remains unaltered. The pieces resulting from the breaking of the pane of glass are just as truly glass as the pane from which they were produced. Similarly, the coal dust obtained by powdering a lump of coal has all the properties of the original coal except size; and the dust as well as the lump may be used as fuel. Changes of this character are termed *physical changes*.

On the other hand, when coal burns, the ash formed is an entirely different kind of matter from the original coal. Similarly, the food that we eat is plainly different from the muscle and bone which are formed through its assimilation in our bodies. We express these facts by saying that in all such changes *the composition of the matter is changed*. Moreover, we shall find that all such changes are attended by an increase or decrease in the available energy associated with the matter. Changes such as these are known as *chemical changes*.

**Definition of chemistry.** In the study of chemistry we shall be interested primarily in those changes in matter which involve a change in composition, that is, in chemical changes. In order to understand these changes it is evident that we must learn a good many facts about the composition of matter; otherwise we cannot understand the changes which it undergoes and the accompanying changes in energy. Chemistry, then, may be defined as *the science which treats of the composition of matter and the changes in composition and energy which matter undergoes*.

**Chemistry, a science.** Thus defined, chemistry is one of the sciences. By the term *science* is meant *a body of knowledge classified in such a way as to make it of value in the search for truth*. It follows that before we ever had a *science* of chemistry a certain amount of knowledge concerning the *facts* of chemistry had to be gained. While chemistry as a science dates back only to the latter part of the eighteenth century, the facts upon which the science was founded had been slowly accumulating throughout the ages of human experience. In truth, some of the facts with which we have to do in chemistry were known long before the beginning of the Christian Era. Thus, several thousand years before the Christian Era, the Egyptians were able to make enamel coatings upon pottery and even to mold glass into vases and flasks; and the art of blowing glass into useful forms dates back to the time of Christ. In the ruins of Pompeii (destroyed A.D. 79 by an eruption of Mt. Vesuvius) has been unearthed what apparently is a small factory for the manufacture of soap. Of course the knowledge of the ancients concerning such materials was very vague and entirely a matter of experience. They had no true conception of the composition of matter, and their discoveries resulted mainly from chance observation.

**The alchemists; alchemy.** For about fifteen centuries following the beginning of the Christian Era the chemists were called *alchemists* (Fig. 1) and the art which they practiced was known as *alchemy*. The fundamental idea which permeated alchemy was the belief in the possibility of transforming one form of matter into another form.

Since alchemy was often practiced in temples by priests, it is sometimes called *the sacred art*; and since the alchemist, as a rule, worked in secret, it is also called *the secret art*. The writings of the alchemists are very vague. They abound in such phrases as *the philosopher's stone*, *the elixir of life*. The former was supposed to have the property of transforming the cheaper metals into gold, while the latter restored health and youth to the aged.



One fundamental belief of alchemy — namely, that it is possible to change the cheaper metals into gold — invited deception, so that some workers in the field of alchemy were dishonest in their claims. Nevertheless many of the alchemists were men of great ability who were entirely honest in their beliefs, and there was nothing then known that made transmutation of the



FIG. 1. An alchemist in his laboratory

metals improbable. The alchemists performed a great many experiments, and in carrying out these experiments many facts of great importance were discovered. It was this knowledge, properly interpreted and classified so as to admit of generalization, that led finally to the birth of chemistry as a science.

**Chemistry a fundamental science.** Since chemistry deals with the composition of matter and the changes it undergoes, it is evident that it is fundamental in character, and a knowledge of it is important in the understanding of most of the other sciences. Thus, in the study of botany we may learn a great



deal about plants and trees without any knowledge of chemistry, and this information is of great importance; but, after all, the most interesting and fundamental problem of the science of botany has to do with *growth*. How is it possible for the growing plant to take a few relatively simple varieties of matter from the soil and the atmosphere and build these up into sugar, starch, and other complex forms of matter which compose the plant? Such a question is primarily a chemical one, and a thorough understanding of the principles of chemistry is necessary for its study. The same is true of physiology, for, among other topics, this science deals with the transformation of the food that we eat into the muscle and bone and other tissues that make up our bodies. Even in astronomy we are interested in the composition of the planets and stars as well as in their motions. With physics the relation is even more intimate, for both physics and chemistry deal with the various forms of energy. Indeed, the relation between physics and chemistry is so intimate that it is impossible to draw any strict dividing line between these two sciences. Some of the most important facts lie in the borderland between these two sciences, and the study of these facts has in recent years given rise to a new science known as *physical chemistry*. Similarly, we have physiological chemistry and biological chemistry.

**The work of the chemist.** Since matter and energy make up the material part of the universe, and since chemistry deals with certain transformations of matter and energy, it may be inferred that the work of the chemist is extensive in scope and of the greatest importance to our personal comfort and our welfare as a nation. It will be of interest for us to note briefly at this time something of the nature of the work the chemist is called upon to perform and the part he plays in the advancement of civilization.

**Two main objects in view.** It should be pointed out first that the work of the chemist, like that of other scientists, has two different objects in view, distinct from each other and yet

closely related: (1) There are many chemists who are interested only in learning the truth and in extending the boundaries of knowledge; (2) other chemists are interested primarily in the application of knowledge to some practical end. Since the discovery of new knowledge and its application to some useful end are so closely associated, it is only natural that most chemists should be interested in both these objects.

**Useful products from raw materials.** It is well for us to note that the raw materials from which are built up, in one way or another, the various commodities which contribute to our well-being come, either directly or indirectly, from natural sources; that is, from the earth or from the organisms living on the earth, or from the atmosphere. But the materials found in nature are rarely in a form adapted to immediate use. Here, then, the chemist plays his part. He separates the metals, such as iron and copper and aluminum, from the ores in which they occur in the earth, and obtains them in pure form adapted to innumerable uses. He transforms certain kinds of rocks into valuable constituents of fertilizers, while from others he prepares such building materials as lime and cement. He separates the crude petroleum, as it flows from the ground, into different constituents, such as gasoline and lubricating oils, adapted to our use. From the growing plant he obtains such products as rubber, turpentine, camphor, quinine, sugar, and starch, and purifies them so that they may be of service to us. In a like way he separates the nitrogen from the air and builds it up into valuable fertilizers.

**Supervision of industry.** But the work of the chemist does not end when he has obtained materials suitable for use in the manufacture of various products. The great percentage of our manufacturing operations are in themselves chemical in their character, for the processes involve certain chemical changes in matter. Whether we are manufacturing glass, or soap, or paints, or fertilizers, or paper, or an automobile, or a hundred other commodities, if the work is to be done efficiently

and economically it is the chemist, associated it is true with workers in related fields of science, who must direct the work. A chemical laboratory is therefore an important part of many manufacturing plants, and hundreds of chemists are employed in the industries. Recent statistics show that there are in the United States more than five hundred industrial laboratories devoted to scientific research.

**Recovery of values from waste products.** The chemist also renders great service by finding out ways of transforming products that are only a source of expense to industry into other products of commercial value. For example, sixty years ago cotton seeds were regarded as a refuse to be disposed of with as little cost as possible. The chemist found that these seeds contained a valuable oil, and the cottonseed-oil industry developed until at present the annual production of oil, together with other materials obtained along with the oil from the seed, has a value of over \$150,000,000.

Similarly, the chemist took the black, tarry mass which is formed when gas and coke are made from coal, and from it prepared thousands of dyes of every imaginable color, valuable medicines, explosives, flavoring agents, and many other products of the greatest importance. Many chemists are employed in work of this character; in fact, many hundreds of chemists are employed in our dye factories alone.

**Preservation of health.** The chemist plays an important part in maintaining the health of the nation. Thus, he studies the composition of our foods and determines what ones are best adapted to our bodies under various conditions. He tests the foods sold on the market to see that they are pure. He devises methods for purifying our water supplies and watches over purification processes wherever installed, and in this way diminishes the spread of certain contagious diseases such as typhoid fever. He transforms materials that would become a menace to health, such as garbage, into useful products. He produces compounds of the greatest service in combating

diseases. In these and many other ways he contributes his share toward preserving the health of the nation.

**Work as teacher.** Finally, many chemists are employed as teachers in our secondary schools and colleges. The great value of chemistry in the advancement of our civilization is becoming more and more apparent, and the demand for well-trained chemists is steadily greater. As a result, the number of students of chemistry is constantly increasing. This work is of the greatest importance. Indeed, it may be said that the industrial advancement of a nation can be judged fairly well by the extent to which chemistry is effectively taught in its schools and colleges.

These examples are sufficient to show something of the varied work of the chemist and of its importance. It is evident that a large number of chemists is necessary to carry on this work. The American Chemical Society is the largest scientific society in the world, having a membership of about 15,000.

**Chemistry still in its infancy.** While the number of workers in the field of chemistry is large, and the increase of our knowledge, especially within recent years, has been very remarkable, it must not be inferred that there is little left to learn or that the future promises little to the energetic chemist. The very opposite is true. Nature is very clever in hiding her secrets from us, and we have made only a good beginning in winning a few of them from her. It is only within the last decade that we have begun to understand a little about the real structure of matter, and we know even less about energy. Questions are constantly arising which as yet we cannot answer, and problems which we cannot solve, but the answers and the solutions will be known sometime. How is the food transformed in our bodies into muscle and bone and other tissues? How does the plant, from simple materials in the soil and the air, build up the complex sugars and starches? To what shall we turn when our supply of petroleum is exhausted, for geologists tell us this will happen within the life

of some who study this book? Our coal will last longer than that, but it is not inexhaustible. What shall we use in its stead as a source of energy? What shall we use in place of lumber when the forests are all gone? Chemists are busily working on these and a hundred equally important problems, and for every problem solved there will be many others pressing for solution. The future is inexhaustible for those who are willing to devote their lives to the study of chemistry, and their discoveries will be of great benefit to mankind. The problems are fascinating in their interest, and the rewards to be secured are very great.



## CHAPTER II

### MATTER AND ENERGY; VARIETIES OF MATTER

**Matter ; weight and mass.** In Chapter I matter was defined tentatively as anything which has mass. Another characteristic of matter is *inertia*. By this is meant that a material body at rest tends to remain at rest, and a material body in motion tends to remain in motion, unless acted upon by some external force. *Mass and inertia*, then, are the two chief characteristics that all kinds of matter have in common.

The terms *mass* and *weight* as applied to matter are closely related but not identical. The *weight* of a body is really the *measure of the earth's attraction for the body*. Thus we may determine the relative weights of different bodies by attaching them successively to a spring balance and noting the points to which the spring is stretched. The one which is attracted most by gravity stretches the spring most and has the greatest weight. By the term *mass*, on the other hand, is meant *that property of a body which determines the acceleration (that is, the rate of change of velocity) that it will acquire when acted upon by a given force*. The less the mass of a body, the greater will be the acceleration for the same force. Thus, a given force applied to a cube of lead and to one of wood, both of the same dimensions and free to move, will impart to the wood a greater acceleration than to the lead; in other words, the mass of the wood is less than the mass of the lead.

**Weight proportional to mass.** If the force of gravity were constant at all points on the earth, we could make use of this force to measure mass directly and should not need to make a distinction between mass and weight; but this is not the fact. If, however, two bodies have the same weight in one locality, they will

have equal weights in all other localities; for if the force of gravity has changed, the change will affect both bodies equally. Consequently the weights of two bodies are always *proportional* to their masses, and it is only occasionally that we need to keep in mind the distinction between the two terms.

**Properties of matter.** By the term *property* as applied to any given form of matter we mean a *mark or characteristic by which we identify that particular kind of matter*. Each form of matter has many properties peculiar to itself, such as its physical state (solid, liquid, or gas), its hardness, density, color, odor, taste, and shape. Thus, sugar is an odorless white solid and has a sweet taste. Common salt is also an odorless white solid, but it differs from sugar in other properties, such as density and taste. While different forms of matter possess different properties, yet they all possess mass and inertia, for mass and inertia are the two characteristics common to all kinds of matter.

**Law of conservation of matter.** Our everyday experience teaches us that matter may be changed from one form into another. Thus, the solid ice is easily changed into liquid water, and this into gaseous steam. Sugar, when heated, gives off liquids and leaves a black residue of carbon. The question naturally arises whether there is any increase or decrease in the mass of the matter as a result of these changes. Much careful experimenting has shown that there is not. The mass of the products formed in any change in matter always equals the mass of the substances undergoing change. We may alter the form of matter, but not its mass. The important truth, known as *the law of the conservation of matter*, or sometimes as *the law of the conservation of mass*, may be stated thus: *In any changes to which we may subject a given quantity of matter the mass remains unchanged.*

**Forms of energy.** We sometimes say of a man that he is full of energy, meaning that he has a great capacity for work. Indeed, we have defined energy (p. 1) as ability to do work.



We recognize this same capacity for work in inanimate things. Steam, highly compressed in a boiler, possesses energy, for on being admitted to the cylinder of a locomotive it will push back the piston and move the train. Energy is present in electrical power lines, for through the necessary mechanical devices we can obtain power, heat, and light from this source. A moving body possesses kinetic energy, and if the body is suddenly stopped, this energy appears as heat.

**Conservation of energy.** The experience gained in a century of experimenting has convinced scientists that *it is impossible to alter the quantity of energy in a system of bodies, save as we add energy from without or allow it to escape from the system*, and this generalization is known as *the law of the conservation of energy*. It is not difficult, however, to transfer energy from one body to another. If a piece of hot metal is dipped into water, the metal is cooled and the water is heated, so that the metal loses energy and the water gains it. When a swinging bat strikes the ball, the ball gains energy while the bat loses it. It is evident, therefore, that a given body does not possess a constant quantity of energy as it possesses constant mass.

**Transformation of energy.** Moreover, energy can be freely transformed from one kind into another. The heat energy of burning coal can be changed into the kinetic energy of the locomotive. The kinetic energy of falling water can be transformed into electrical energy, as in the power plants of Niagara Falls. The electrical energy of the trolley line is readily converted into the kinetic energy of the moving car and the light energy of the electric lamps. In all such transformations *a definite quantity of energy of one kind always gives a definite quantity of another*, so that we speak of the mechanical equivalent of heat, or of the electrical equivalent of mechanical energy. The diagram (Fig. 2) illustrates a few familiar transformations of energy.

**Chemical energy.** A body may possess energy that is due to its motion or to its position. A piece of coal, however,

possesses energy due neither to its motion nor to its position but to its ability to undergo combustion, for in this process both heat and light are evolved. Our experience leads us to believe that this heat and light must have come from some other form of energy present in the coal and the oxygen, which unite in the process of burning. This form of energy

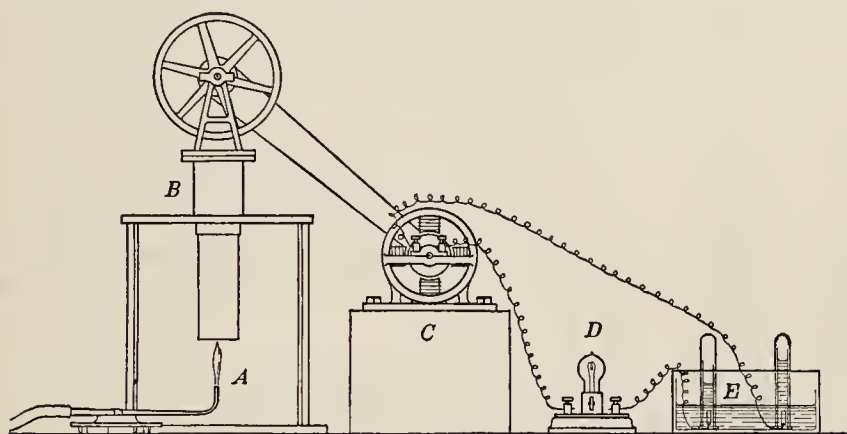


FIG. 2. Diagram illustrating some transformations of energy

The heat of the flame *A* is converted into mechanical energy in the heat engine *B*. The motion of the engine is communicated to the small dynamo *C*, where it is converted into magnetic and electrical energy. The electrical energy is changed into heat and light in the incandescent lamp *D*, and into chemical energy by the decomposition of water in the vessel *E*

is called *chemical energy*. It is the form possessed by substances which enables them to undergo changes similar to combustion, and it is the form of energy in which the chemist is especially interested.

**The measurement of energy.** Since changes in energy are so constantly taking place all about us, it is a matter of great practical importance to devise units for the measurement of energy, and methods for making the measurement. In general, each kind of energy must have its own units of measurement, just as with matter we have centimeters for lengths, liters for volumes, and grams for weights. In some of its forms energy is very difficult to measure directly, and neither units

nor methods for the direct measurement of chemical energy have as yet been devised. In such cases it is necessary to transform the energy into a form more convenient for measurement. In the case of chemical energy it is changed into heat or electrical energy for this purpose.

**Measurement of heat.** A quantity of heat energy is measured by observing to what extent it will change the temperature of a given mass of some standard substance. Water has

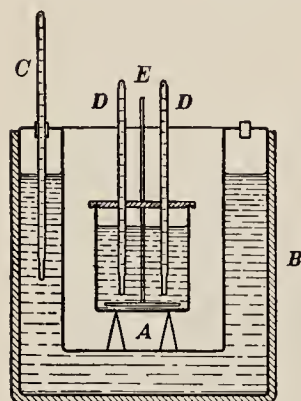


FIG. 3. A simple calorimeter

been chosen as the standard, and the unit of heat is called the *calorie* (designated by the abbreviation *cal.*). It is defined as *the quantity of heat required to change the temperature of one gram of water one degree on the centigrade scale.*

**The calorimeter.** The actual measurement of the quantity of chemical energy transformed into heat in any definite change is accomplished by the use of an apparatus called the *calorimeter*, a simple form of which is represented in Fig. 3.

The change is arranged to take place in solution in a measured volume of water contained in a thin-walled metal vessel *A*. This is placed within a double-walled vessel *B*, which contains water at the temperature of the room. The thermometer *C* indicates when the water has reached this temperature. This water is to prevent the influence of heat from without, and as an added precaution the vessel is covered with a thick layer of nonconducting felt. The heat evolved by the change raises the temperature of the solution, the rise being indicated by the thermometers *D, D*. During the change the solution is stirred by the stirrer *E*. If the weight of the water is (say) 2570 grams and the rise in temperature is  $1.5^{\circ}$  centigrade, the heat evolved is  $2570 \times 1.5 = 3855$  cal.

**Units used and their abbreviations.** All temperature readings given in the following pages are those of the centigrade scale unless a definite statement is made to the contrary.

In referring to other units of measurements the commonly accepted abbreviations will be employed, such as g. for gram, kg. for kilogram, cc. for cubic centimeter, and lb. for pound.

**Varieties of matter.** The variety of forms which matter assumes in all the wonderful transformations of nature is almost infinite, and these forms may be classified in a great many ways, according to the purpose in view. The interest of the chemist *centers chiefly in the composition of substances and in their chemical energy*, together with the changes which take place in both of these. From this standpoint he finds it convenient to arrange matter in three groups: namely, *compounds, elements, and mixtures*.

**Illustrative experiments.** The distinction between these three classes can best be explained by the following illustrative experiments.

**Experiment 1.** The chief properties of the substances iron and sulfur are familiar to almost everyone. Iron filings form a heavy gray powder, strongly attracted by the magnet. When treated with the liquid known as hydrochloric acid the iron passes into solution and an odorless gas called hydrogen is evolved, considerable heat being liberated in the process. Sulfur is ordinarily obtained as a light-yellow powder not attracted by a magnet or dissolved by hydrochloric acid. It is readily soluble in the liquid known as carbon disulfide, however, while iron is not soluble; and when the solution is allowed to evaporate, the sulfur is deposited in the form of yellow crystals.

When iron filings and sulfur are thoroughly ground together, a greenish-black powder is obtained which in appearance is quite different from either of them; but when we apply the tests which characterize iron and sulfur, it is found that in many respects the powder acts like these two taken separately. Hydrochloric acid still dissolves the iron and evolves hydrogen with the same heat as before, leaving the sulfur unchanged. A magnet rubbed through the material withdraws the iron and leaves the sulfur. Carbon disulfide dissolves the sulfur but



not the iron. The sulfur and the iron each act just as they did before they were ground together, and with the same energy.

If, now, a portion of the powder is placed in a test tube and heated, as shown in Fig. 4, it soon begins to glow at the point of greatest heat; and even if the flame is withdrawn, the glow continues to spread throughout the entire contents of the test tube, and a great deal of heat is set free at the same time.

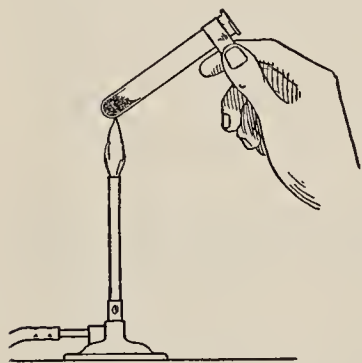


FIG. 4. Heating a mixture of iron and sulfur

When the product is examined, it is found that many of the characteristics of the iron and sulfur have been modified. Carbon disulfide no longer dissolves sulfur and leaves iron; a magnet has no effect upon the material; hydrochloric acid dissolves the entire product and evolves a gas of disagreeable odor quite different from hydrogen; and the heat liberated is different in quantity from that in the former case.

The new product also differs from the iron and the sulfur in density, color, hardness, solubility, and melting point. This new product which is formed by the union of iron and sulfur is called *iron sulfide*.

**Experiment 2.** When a small quantity of sugar is heated in a test tube, it melts, turns brown in color, gives off vapors, and finally dries up to a solid black residue which may be identified as *carbon*. By collecting and examining the vapors it is possible to show that they are largely water. To make this transformation complete it is necessary to apply heat throughout the entire process. In this experiment one substance, merely by the application of heat, has given rise to two others of very different properties, and the change is described as a *decomposition*.

**Chemical reactions.** The two experiments that have just been described are very different in many ways, but they have

several characteristics in common. Most of the properties of the materials concerned undergo a very considerable change, so that the products formed are different from the original materials. A more important characteristic is that *the chemical energy of the materials has been changed*. The action of iron with sulfur, when once started, is attended by the evolution of a great deal of heat, and this is at the expense of the chemical energy of the original substances. To effect the decomposition of sugar it is necessary to supply heat during the entire period of decomposition, and this heat must be converted into some other form of energy. A part of it is converted into chemical energy, so that the carbon and the water taken together represent more energy of this kind than does the original sugar. *Any change in the composition of matter that involves a change in the chemical energy of the substances concerned is called a chemical action or a chemical reaction.*

**Definition of chemical compounds.** *When it can be shown that a substance is composed of at least two different materials, and that its chemical energy is different from that of the constituents taken separately, it is called a chemical compound.* Thus, we judge iron sulfide to be a chemical compound, for it contains iron and sulfur and yet differs from them in chemical energy. It is not always a simple matter to determine whether a given material is a chemical compound or not. We are assisted in our decision by the fact, to be proved in a later chapter, that *the percentage composition of a given compound is always the same*. Thus, iron sulfide always contains 63.52 per cent iron and 36.48 per cent sulfur. If the material can be obtained in pure form and analyzed, it is usually possible to decide whether or not it is a compound by the constancy of its composition.

**Chemical affinity.** It is important to distinguish clearly between chemical action and the force that brings about the action. This force is called *chemical affinity*. For example, we say that iron and sulfur combine because of their chemical

affinity. We can form little idea, as yet, as to the nature of this force, just as we have little idea as to the nature of the force of gravitation. In both cases we merely give names to forces which we must believe to be acting.

**Conditions affecting chemical action.** There are many conditions which may either promote or hinder chemical action. An increase in temperature is usually favorable to chemical action, as was seen in the case of iron and sulfur. It frequently promotes decomposition, as in the case of sugar. Other forms of energy, such as light, mechanical pressure, shock, and electrical energy, may also facilitate either chemical union or decomposition, at times overcoming obstacles which prevent union, in other cases overpowering the chemical affinity which holds a compound together.

**Chemical conduct of substances.** Substances differ very greatly from each other in the way in which they act toward other substances. Thus, a substance may burn with a flame when heated in the air, or it may combine with another substance with incandescence, as is the case of iron heated with sulfur. It may decompose when heated, as is true of sugar, or when subjected to the action of the electric current, as water does. All such peculiarities are collectively called the *chemical conduct* of a substance.

**Decomposition of substances.** We have seen that sugar can be decomposed into two different substances, namely, water and carbon. The question naturally arises whether or not the water and carbon, as well as other forms of matter, such as iron and sulfur, can likewise be decomposed into other substances. To determine whether or not any given substance can be decomposed, we may heat the substance, as in the case of sugar; or we may employ other agencies. For example, experience has shown that in many cases decomposition may be brought about by the electrical current or by the action of substances possessed of great chemical energy, and we may also employ these methods. In such ways chemists have succeeded



in decomposing water into two invisible gases, oxygen and hydrogen, so that water must be regarded as a compound.

On the other hand, carbon, iron, and sulfur have never been decomposed, notwithstanding the many efforts directed to this end.

**The decomposition of water.** The decomposition of water may readily be observed by the aid of an apparatus such as that represented in Fig. 5. Two test tubes, *A* and *B*, are filled with water and inverted in a vessel half filled with water to which a little sulfuric acid has been added. A piece of platinum foil, *C* and *D*, attached to a wire is then brought under the end of each tube. When these wires are connected with a source of current supplying from 6 to 10 volts, bubbles of gas will be seen to form in each tube. These gases may be shown to have different properties; they are hydrogen and oxygen. The reason for adding the sulfuric acid will be discussed later.

**Elements.** We conclude, therefore, that there are a limited number of substances out of which all compounds have been formed, and which are not decomposed into simpler forms of matter in any ordinary process of nature or laboratory experiment. Such simple substances are called *elements* or *elementary substances*. Among these are oxygen, hydrogen, carbon, sulfur, and iron.

**Elements not simple units.** In recent years it has been demonstrated that, in some way which we do not understand, the elements themselves have been formed by the condensation of two really primitive units, namely, positive and negative electricity. The positive electrical unit is closely related to the two gases hydrogen and helium, and a few of the elements, such as uranium and thorium, are very slowly decomposing, yielding helium in the process.

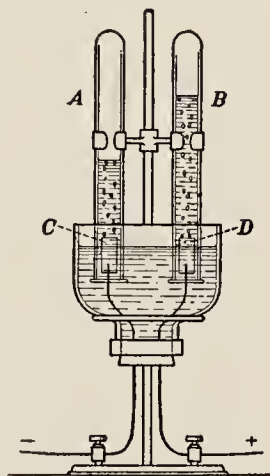


FIG. 5. The decomposition of water into oxygen and hydrogen by the electric current

Tremendous energy is liberated in this decomposition, and when exposed to this energy some well-known elements, such as nitrogen, are knocked to pieces, yielding one or both of these gases. But, so far as we know, all the so-called elements remain unchanged by any ordinary process of nature and during chemical combination or decomposition, and so for all practical purposes we may regard them as the unchanging units out of which all compounds are built up.

**Number of the elements.** While many thousands of compounds have been described, the number of the elements at present known is comparatively small; that is, ninety. For reasons to be explained later, chemists are reasonably certain that the total number of elements is ninety-two. Only two, therefore, remain to be discovered. Some of these elements have long been known; others have only recently been discovered. The last one announced is *illinium*, which was discovered by the American chemist Hopkins in 1926.

A list of the known elements is given in the table on the inside back cover of this book. Following the name of each element in the table is an abbreviation called a *symbol*, by which the element is designated among chemists. The symbol is usually the initial letter of the name of the element, together with some other characteristic letter. In the case of some of the elements the symbol is the abbreviation of the old Latin name, as is true of iron (*ferrum*), gold (*aurum*), and mercury (*hydrargyrum*). The significance of the columns of numbers will be made clear a little later.

**Physical state of the elements.** About ten of the elements are gases at ordinary temperatures. Two—mercury and bromine—are liquids. The others are all solids, though their melting points vary through wide limits, from cesium, which melts at  $26^{\circ}$ , to elements which do not melt save in the intense heat of the electric furnace.

**Occurrence of the elements.** Comparatively few of the elements occur as uncombined substances in nature, most of them being found in the form of chemical compounds. When an

element does occur by itself, as is the case with gold, we say that it occurs *in the free state* or *native*; when it is combined with other substances in the form of compounds, we say that it occurs *in the combined state* or *in combination*. In the latter case there is usually little about the compound to suggest that the element is present in it, for we have seen that elements lose their own peculiar properties when they enter into combination with other elements. From its appearance it would never be suspected that the reddish, earthy-looking iron ore contains iron or that water contains hydrogen and oxygen.

**Names of the elements.** The names given to the elements have been selected in a great many different ways. (1) Some names are very old and their original meaning is obscure. Such names are *iron*, *gold*, and *copper*. (2) Many names indicate some striking physical property of the element. The name *bromine*, for example, is derived from a Greek word meaning "stench," referring to the extremely unpleasant odor of the substance. (3) Some names indicate the chemical conduct of the elements. Thus, *nitrogen* means "the producer of niter," nitrogen being a constituent of niter, or saltpeter; *argon* means "lazy" or "inert," the element being so named because of its inactivity. (4) Other elements, as germanium and illinium (Illinois), are named from countries or localities. (5) Still others, as tantalum, suggest characters in mythology.

**Distribution of the elements.** So far as we can judge, the elements are of very unequal occurrence in nature. It must be remembered, however, that our knowledge of the earth's composition is confined to what is a comparatively thin surface shell, not exceeding a few miles in thickness. The table below, prepared by F. W. Clarke and based on the analysis of representative rocks and minerals, gives an estimate of the composition of this solid shell. It will be seen that eleven of the elements are estimated to constitute 99.47 per cent of the shell. Some of the elements are of such rare occurrence that only a few milligrams have ever been isolated.

## ESTIMATED COMPOSITION OF THE EARTH'S CRUST

Oxygen . . . . .	46.71%	Potassium . . . . .	2.56%
Silicon . . . . .	27.69%	Magnesium . . . . .	2.08%
Aluminum . . . . .	8.07%	Titanium . . . . .	0.62%
Iron . . . . .	5.05%	Hydrogen . . . . .	0.14%
Calcium . . . . .	3.65%	Phosphorus . . . . .	0.13%
Sodium . . . . .	2.75%	All other elements . . . .	0.53%

**Elements essential to life.** An examination of the materials present in living organisms shows that only a few elements are of vital importance to us. The following table, compiled by Sherman, indicates the average composition of the human body. It is possible that other elements have an importance which we do not realize, but, so far as we can judge, these are the only ones upon which living organisms are dependent.

## AVERAGE COMPOSITION OF THE HUMAN BODY

Oxygen . . . . .	65.00%	Phosphorus . . . . .	1.00%	Magnesium . . . . .	0.05%
Carbon . . . . .	18.00%	Potassium . . . . .	0.35%	Iron . . . . .	0.004%
Hydrogen . . . . .	10.00%	Sulfur . . . . .	0.25%	Iodine, fluorine	} traces
Nitrogen . . . . .	3.00%	Sodium . . . . .	0.15%	and other ele-	
Calcium . . . . .	1.50%	Chlorine . . . . .	0.15%	ments	

**The number of compounds.** The number of compounds which have been described and which can be made when desired is very large, and each year many more are added to the list. More than 200,000 are known that contain the element carbon as one constituent, and the total number listed in the handbooks of chemistry is much larger. Fortunately it is not necessary to become familiar with any great number of these in order to gain an understanding of the principles of chemistry.

**Meaning of the terms *mixture* and *substance*.** We have discussed the nature of elements and compounds and learned something of their characteristics. It is possible for us to mix intimately together many different elements and compounds without any chemical action's taking place. The resulting product is called a *mixture*. Thus, we may have a mixture



of sand and salt or of sugar and flour. Such products differ from compounds in that their composition may be varied indefinitely; moreover, in a typical mixture particles of different character may be distinguished, while in a compound all particles, no matter how minute, are identical in composition and properties. When we wish to refer to some form of matter without regard to its composition, we often use the term *substance*. Thus, we might speak of an element, a compound, or a mixture as a substance.

**Method of study.** We shall now proceed with a study of some of the more important elements. As a rule each element will be discussed under the following heads: (1) *Properties*. By this word is meant all those physical characteristics of a substance by which we recognize it. This includes its state (solid, liquid, or gas), color, odor, and taste. It also includes certain measured quantities such as weight, hardness, solubility, boiling point, freezing point. (2) *Occurrence in nature*. Under this heading will be discussed such topics as the forms in which the element occurs in nature (whether free or in the combined state) and whether it is an abundant element or of rare occurrence. (3) *Historical study*. It is always of interest to know something concerning the discovery of the element. (4) *Preparation*. As a rule the elements do not occur pure in nature but are found mixed or combined with various other substances. It becomes necessary, therefore, to discover methods whereby the elements can be separated from other substances and thus obtained in a pure state. (5) *Chemical conduct*. Under this head will be described the various chemical changes in which the element plays a part, and the methods for producing these changes. In studying oxygen, for example, we shall want to know what other elements will combine with oxygen, the conditions necessary to bring about the combination, and the nature of the resulting products. (6) *Uses*. From a practical standpoint it is important for us to learn about the various uses to which the different elements are adapted.

## EXERCISES

1. Give instances illustrating the law of the conservation of energy and the law of the conservation of matter.

2. The energy of the falling water at Niagara Falls is utilized in propelling, heating, and lighting the trolley cars at Buffalo. Trace the changes of energy involved.

3. What is the source of the energy of the human body?

4. Why does the body become warm with exercise?

5. Trace the energy changes between the coal on the locomotive and the sound of the locomotive whistle that one hears.

6. When a drill cuts a hole in a piece of iron, the drill becomes hot. Where does this heat come from?

7. What are the conditions that favor the chemical reaction in (a) lighting a match? (b) setting off dynamite? (c) taking a photograph?

8. What means of decomposing a compound can you suggest besides heating it?

9. Define a compound; an element. Which group is the more numerous?

10. Does the fact that a substance undergoes no change on being heated show it to be an element?

11. Read over the list of elements. What ones do you know to occur native?

12. Aluminum is much more abundant than iron (see Clarke's table). How do you account for the much greater cheapness of iron?

13. Consult the dictionary for the derivation and significance of the names of the following elements: phosphorus, hydrogen, germanium, columbium, chlorine, argon, copper, selenium, thorium, iodine.

14. Give examples of chemical action caused through the agency of heat; of light; of electricity.

15. The fuel value of a certain kind of coal was determined by burning 1 g. of the coal in a calorimeter containing 2500 g. of water. The heat liberated raised the temperature of the water  $1.5^{\circ}$ . Calculate the number of calories of heat evolved by the burning of the coal.

16. A certain fuel gives out 4000 cal. per gram when burned. What weight of it would be required to heat 3 liters of water from room temperature ( $18^{\circ}$ ) to the boiling point, supposing that all the heat evolved is used in raising the temperature of the water?



## CHAPTER III

### OXYGEN

**Introduction.** In the preceding chapters we have learned something of the meaning of the terms *matter* and *energy*. We have seen also that matter may exist either in the form of elements or in the form of chemical compounds or mixtures, and we have become acquainted with a few of the characteristics of the elements as a class. We shall now turn to a detailed study of some of the more common of the elements. It is but natural that we should begin with oxygen and hydrogen. Oxygen is the most abundant of all elements, occurs uncombined in large quantities in the air, and plays an important part in such fundamental processes as combustion and respiration. Combined with hydrogen it forms water. These two elements, oxygen and hydrogen, are both colorless, odorless gases, but they differ widely in their chemical conduct.

**Properties of oxygen.** Oxygen is a colorless, odorless, tasteless gas, slightly heavier than air. One liter of it, measured at a temperature of  $0^{\circ}$  and under a pressure of 1 atmosphere, weighs 1.429 g., while under similar conditions 1 liter of air weighs 1.2928 g. It is but slightly soluble in water, 100 volumes of water at  $0^{\circ}$  dissolving approximately 5 volumes of the gas under ordinary atmospheric pressure. Oxygen, like other gases, may be liquefied by applying very great pressure to the highly cooled gas. When the pressure is removed, the liquid oxygen passes again into the gaseous state, since its boiling point under ordinary atmospheric pressure is  $-183^{\circ}$ . By reducing the temperature still lower oxygen is obtained in the form of a snowlike solid which melts at  $-218.4^{\circ}$ . For

purposes of transportation the gas is pumped under great pressure into strong steel cylinders (Fig. 6), and it may be purchased in this form.

It is a well-known fact that gases expand on heating; also that the weight of a gas that occupies a certain volume (say, that of a given automobile tire) may be greatly increased by pressure. It is evident, therefore, that the weight of a given volume of any gas will vary with the temperature and pressure under which the

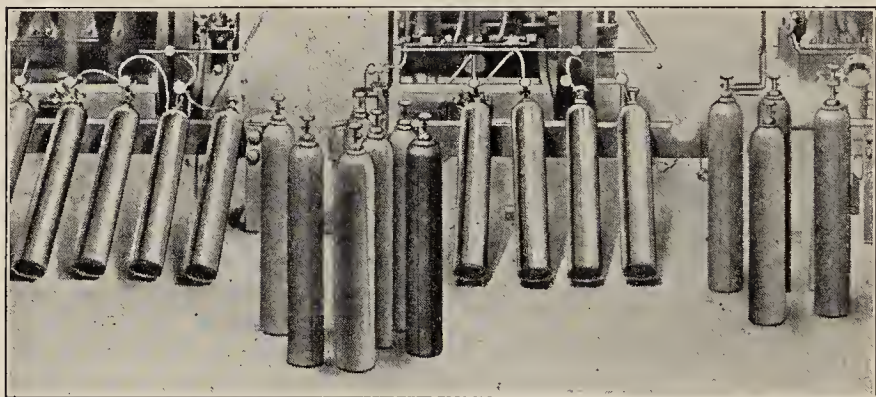


FIG. 6. Oxygen stored in steel cylinders. In this form it is sold on the market

gas is measured. In order to avoid confusion, chemists have agreed upon a standard temperature and a standard pressure, namely, a temperature of  $0^{\circ}$  and a pressure equal to the average pressure exerted by the atmosphere at sea level (1033 g. per square centimeter). In giving the weight of a given volume of any gas it will be understood, unless otherwise stated, that the gas is measured under these standard conditions of temperature and pressure.

**Occurrence.** Oxygen is by far the most abundant of all the elements. It occurs both in the free state and in combination. In the free state it is found in the air, 100 volumes of *dry* air containing about 21 volumes of oxygen. In the combined state it forms 88.81 per cent by weight of water and nearly one half of the rocks composing the earth's crust. It is also an important constituent of the compounds (including water)

that compose plant and animal tissues ; for example, about two thirds, by weight, of the human body is oxygen (consult tables on page 22).

**Historical.** The discovery of oxygen is attributed to the English chemist Priestley (Fig. 7), who in 1774 obtained the element by heating a compound of mercury and oxygen now known as red oxide of mercury. It is known, however, that other investigators, especially the Swedish chemist Scheele, had obtained it at an earlier date, but failed to attract attention to their discovery. The name *oxygen* signifies "acid former." It was given to the element by the French chemist Lavoisier (Frontispiece), since he believed that all acids owe their characteristic properties to the presence of oxygen. This idea we now know to be incorrect, for many acids do not contain oxygen.

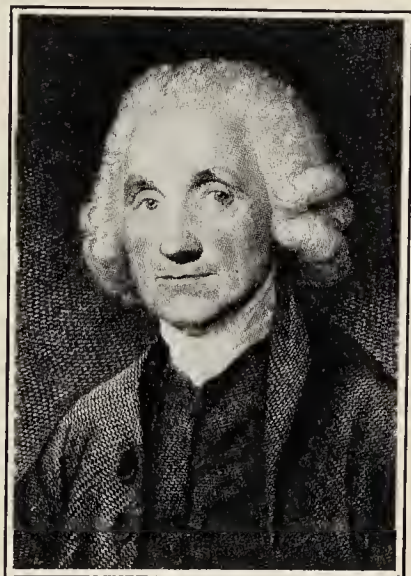


FIG. 7. Joseph Priestley  
(1733-1804)

The discoverer of oxygen

Priestley was born near Leeds, England, in 1733. He was educated for the ministry and all his life followed that profession, but he became interested in science and spent much of his spare time in performing experiments. In 1774, while studying gases, or "airs," as he called them, he heated the compound now known as mercuric oxide by means of a large burning-glass and found that a colorless gas was evolved. This gas, which Lavoisier later named oxygen, attracted his attention because a candle burned in it with a brilliant flame. Later Priestley had to leave England because of his liberal views. He came to America in 1794 and settled in Northumberland, Pennsylvania, where he resided until his death in 1804. The house in which he lived still stands and is preserved as a memorial to him.

**Preparation.** While oxygen is very abundant, it does not occur in nature in a pure condition. To obtain pure oxygen we must either liberate it from some compound or separate it from the gases with which it is mixed in the air. The most important of the methods for preparing the pure element are the following:

1. *Preparation from water.* Water is a compound, consisting of 88.81 per cent oxygen and 11.19 per cent hydrogen. It is easily separated into these constituents by passing an electric current through it, as has already been explained (p. 19).

2. *Preparation by heating certain compounds of oxygen.* Some of the compounds of oxygen, when heated, give off at least a portion of their oxygen. For example, mercuric oxide, a solid compound containing 7.39 per cent of oxygen and 92.61 per cent of mercury, is decomposed into its elements by heating it. The change may be represented in the following way, in which the names of the elements composing the compound are inclosed in brackets just beneath the name of the compound:

mercuric oxide  $\longrightarrow$  mercury + oxygen

[mercury]  
[oxygen]

The compound best adapted to the preparation of oxygen by this method is *potassium chlorate*. This compound is a white solid containing 39.16 per cent of oxygen, 31.90 per cent of potassium, and 28.94 per cent of chlorine. When heated it undergoes a series of changes in which all the oxygen is finally set free, leaving a white solid compound of potassium and chlorine called *potassium chloride*. The change may be represented as follows:

potassium chlorate  $\longrightarrow$  potassium chloride + oxygen

[potassium]  
[chlorine]  
[oxygen]

[potassium]  
[chlorine]

The evolution of the gas becomes marked at about 400°.

It is a remarkable fact that the rate at which oxygen is evolved at any given temperature is greatly increased by the



presence of small quantities of certain substances, notably *manganese dioxide*. By mixing such a substance with the chlorate it is possible, therefore, to obtain oxygen rapidly at a lower temperature than would otherwise have to be employed. As to the way in which the manganese dioxide promotes the decomposition, it may be said at once that we do not know. Apparently it undergoes no change during the reaction; at least there is exactly the same weight of it present when the reaction is completed as when it began. Certainly

it contributes no oxygen, for the weight of oxygen obtained is always 39.16 per cent of the weight of the chlorate used, irrespective of the presence of manganese dioxide. This is but one example

of many in which the rate of change is influenced by an apparently inactive substance. Such materials are called *catalyzers*, and the process involving

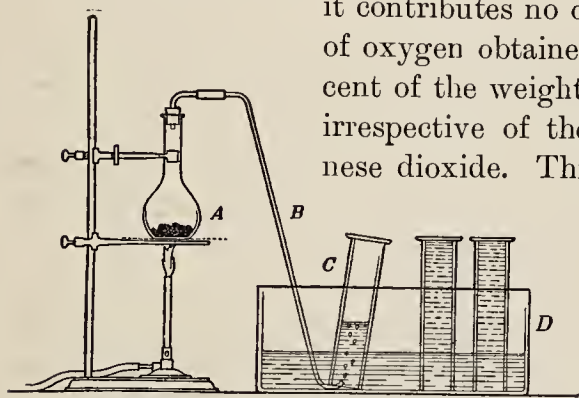


FIG. 8. Preparation of oxygen from potassium chlorate, and method of collecting the gas

their use is called *catalysis*. We shall meet with these substances frequently in subsequent pages, since a great many chemical processes depend upon suitable catalyzers for their success.

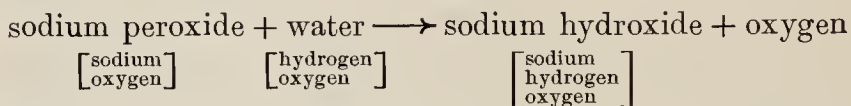
**Laboratory preparation of oxygen.** The preparation of oxygen from potassium chlorate as commonly carried out in the laboratory is as follows:

The potassium chlorate, mixed with about one fourth of its weight of manganese dioxide, is placed in a suitable vessel, such as a glass flask, which is provided with a stopper and glass tube, as shown in *A* (Fig. 8). A gentle heat is applied and oxygen is evolved and passes out through the tube *B*. It is evident that the oxygen which first escapes is mixed with the air contained in the flask. In a short time, as the evolution of oxygen continues, all



this air is displaced, and the pure oxygen may then be collected by bringing the end of the delivery tube under the mouth of a glass cylinder *C*, which has been filled with water and inverted in a trough of water *D*, as shown in the figure. The gas rises in the cylinder and displaces the water.

3. *Preparation from sodium peroxide.* This compound is a white solid containing 41.02 per cent of oxygen. When water is brought into contact with it the two react in such a way as to liberate a portion of the oxygen. This reaction may be expressed as follows:



While this is an expensive method, it is often used because of its simplicity. It is only necessary to bring the two compounds together in order to obtain the gas.

4. *Preparation from air.* Since air contains such a large percentage of free oxygen, one would naturally expect methods to be devised for obtaining oxygen from this source. The problem is not so simple as it may seem, for there are other gases in the air, and the separation of a gas in pure condition from a mixture of gases is always difficult.

To accomplish the separation the air is first subjected to the combined effects of pressure and low temperature. In this way it is possible to obtain liquid air, which is essentially a mixture of oxygen and nitrogen in the liquid state. When this liquid is allowed to stand under ordinary pressure, it boils rapidly and its temperature falls to a very low point. Since nitrogen has the lower boiling point ( $-195.8^{\circ}$ ), it tends to boil away first; it is gradually followed by the oxygen (boiling point,  $-183^{\circ}$ ), which may be collected separately. Prepared in this way the oxygen usually contains some nitrogen.

**Laboratory and commercial methods of preparation.** We have seen that a number of different methods may be used for the preparation of oxygen. We shall find as we proceed

that this is true in reference to most of the other elements. Some of these methods are expensive, while others necessitate the use of complicated apparatus or costly machinery. For the purpose of laboratory experiments, in which relatively small quantities are desired, the choice of the method will naturally be decided by convenience and simplicity of apparatus, while in the preparation on a commercial scale economy will determine the method. In the case of oxygen the method of preparation from potassium chlorate has proved itself the most suitable for laboratory purposes. For commercial purposes oxygen is obtained chiefly from air (method 4); small quantities are prepared by decomposing water with the electric current (method 1).

**Chemical conduct.** At ordinary temperatures oxygen is not very active; most substances either are not affected by it or are affected so slowly that the action escapes notice. At higher temperatures, however, oxygen is very active and unites directly with most of the elements. This may be shown by heating various substances until they are just ignited in air, and then bringing them into vessels containing oxygen, when they burn with greatly increased brilliancy. Thus, a glowing splint of wood introduced into a jar of oxygen bursts into flame. Sulfur burns in air with a very weak flame and a feeble light; in oxygen the flame is increased in size and brightness (Fig. 9). Substances which burn readily in the air, such as phosphorus, burn in oxygen with dazzling brilliancy. Many substances which burn in the air with great difficulty, such as iron, burn readily in oxygen.

**The nature of the action of oxygen upon substances.** It is possible to show by experiment that the action of oxygen upon another element consists in the union of the two

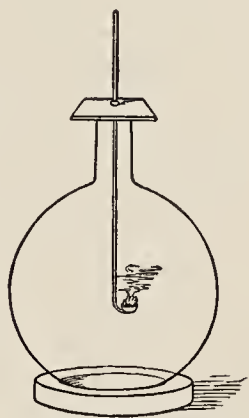


FIG. 9. Burning sulfur in oxygen

elements to form a compound. Thus, when sulfur burns in oxygen, both sulfur and oxygen disappear as such, and in their place we find a gaseous compound composed of the two elements. Likewise, when phosphorus or iron or carbon burn in oxygen, compounds of these elements with oxygen are formed. Many compounds as well as elements burn readily both in air and in oxygen; among these are the compounds present in coal, wood, oil, and gas. In the majority of such cases the compound is completely decomposed and each of its constituent elements combines with oxygen. Thus, most oils are compounds of carbon and hydrogen, and when the oil burns there are formed a compound of carbon and oxygen (carbon dioxide) and a compound of hydrogen and oxygen (water). Less frequently the compound undergoes no decomposition, but merely as a whole combines with oxygen.

**Oxidation; oxidizing agent.** The general term *oxidation* is applied to all such processes as those described above, in which *any substance or its constituent parts combines with oxygen*. Thus, we speak of the oxidation of phosphorus or sulfur or wood by the air or by pure oxygen, and we say that these substances readily undergo oxidation. The material which supplies the oxygen is called the *oxidizing agent*. In the examples just mentioned the air or pure oxygen is the oxidizing agent, but in many cases the oxygen is supplied by some compound, such as potassium chlorate or sodium peroxide. We shall find later that the term *oxidation* is not confined to such changes as those just mentioned, but has a much broader application. For the present, however, it will be used in the sense explained.

**Oxides; products of oxidation.** When any element combines with oxygen, the resulting compound is known as an *oxide* of that element. Thus, the compound formed by the union of sulfur with oxygen is known as an oxide of sulfur. Likewise, when phosphorus or iron or carbon combines with oxygen, the resulting compounds formed are oxides. The

particular oxide or oxides formed in the oxidation of any substance are known in general as the *products of oxidation* of that substance. Thus, sulfur dioxide is the product of oxidation of sulfur, and carbon dioxide is the product of oxidation of carbon.

**Physical state of oxides.** Oxides of nearly all the elements have been prepared, and they constitute an important class of compounds. Some of these oxides are invisible gases, as is true of the oxides of sulfur and of carbon. In a few cases the oxide is a liquid, the most familiar example being water, which is an oxide of hydrogen. In the great majority of cases, however, the oxides are solids, which is true of those of iron and phosphorus. It is easy to understand, therefore, why such elements as sulfur and carbon completely vanish on burning, leaving no ash, while other elements, such as iron and phosphorus, leave a solid residue.

**Combustion.** Experiments have shown that heat is evolved when a substance combines directly with oxygen. Equal weights of different substances evolve different amounts of heat on oxidation, but *for the same substances a given weight will always evolve the same amount of heat*, no matter whether the process of oxidation takes place rapidly or slowly, provided only that the products of oxidation are the same. When the process takes place slowly, so little heat is evolved at any moment that it is not noticed, although it can be detected by the use of delicate instruments. If, on the other hand, the process takes place rapidly, so much heat is evolved in a short period that it may cause the substance to glow or burst into a flame. In such a case the substance is said to undergo *combustion*, and the products formed are referred to as the *products of combustion* of the substance. In its broad sense *the term combustion is applied to any chemical reaction in which light is evolved*. The most familiar examples of combustion, however, are those in which the substance burns in air or oxygen, and which are therefore oxidations. Ordinarily, when we speak of a combustible substance, we mean one that will burn in air or oxygen.



**Weight relations in oxidation.** If it is true that oxidation (including combustion) is essentially the union of oxygen with other elements or compounds, it must necessarily follow that the weight of the product formed is greater than that of the substance oxidized or burned, although our common experience with fuels would hardly lead us to such a conclusion. That the weight does increase may be demonstrated by arranging an experiment in which the oxidation takes place on one pan of a balance.

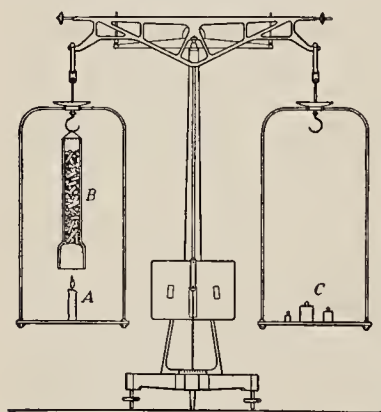


FIG. 10. Demonstration of increase in weight during burning

may be placed in a small porcelain dish and accurately counterpoised on the balance. The iron may then be ignited by directing a hot flame upon it. As the oxidation proceeds, it will be seen that the scale pan supporting the dish sinks. A modification of this experiment will show a similar gain in weight during the burning of a candle.

**Increase in weight of a burning candle.**

The candle is arranged on a balance pan shown in Fig. 10. Over it is suspended a wide glass tube (a lamp chimney) loosely filled with sticks of sodium hydroxide, a substance which will absorb both water and oxide of carbon. When the whole apparatus has been brought to an equilibrium on the balance, the candle is lighted. The heat and light are the result of the oxidation of the carbon and hydrogen present in the compounds making up the candle. The products of this oxidation are oxide of carbon and oxide of hydrogen (water). The oxide of carbon formed is commonly known as *carbon dioxide* and is a gas even at ordinary temperatures, while the water formed is also gaseous in form at the temperature of combustion. Both of these products are drawn up through the chimney and absorbed by the sodium hydroxide. The balance pan sinks as the oxidation progresses, indicating an increase in weight.



**Spontaneous combustion.** It has been found that the rate at which oxidation goes on is greatly increased by raising the temperature of the material undergoing oxidation. Consequently, if the conditions surrounding oxidation are such that the heat given off cannot escape, the temperature will steadily rise, and because of this the rate of oxidation will increase. The increased heat thus set free will still further raise the temperature, until the oxidation passes into active combustion, the point at which this occurs being called the *kindling temperature*. Materials taking fire in this way are said to undergo *spontaneous combustion*. It will be seen that the essential conditions are (1) an existing oxidation and (2) good heat insulation. Linseed oil, used in paints, undergoes rather rapid oxidation in air, and oily rags left by painters not infrequently occasion disastrous fires. Fine coal in the center of a heap or in the closed hold of a vessel sometimes takes fire. Almost any finely divided combustible material, such as sawdust or flour, is dangerous when stored in a warm, dry place. Sometimes the heat of fermentation, which is a kind of oxidation, will start a fire in a haystack or barn if the hay is not well dried before being stored.

**Phlogiston theory of combustion.** The French chemist Lavoisier (1743-1794), who gave to oxygen its name, was the first to show that combustion is due to union with oxygen. This must be regarded as one of the greatest of chemical discoveries, and it was this discovery, more than any other, which raised chemistry to the dignity of a science. Previous to Lavoisier's discovery, combustion was supposed to be due to the presence of a substance or principle called *phlogiston*. One substance was thought to be more combustible than another because it contained more phlogiston. For example, coal was thought to be very rich in phlogiston. The ashes left after combustion would not burn, because all the phlogiston had escaped. If the phlogiston were to be restored in any way, the substance would then become again combustible. Although this view seems absurd to us in the light of our present knowledge, it formerly had general acceptance. .

The discovery of oxygen led Lavoisier to investigate the subject. He placed some mercury in a retort *A* (Fig. 11) and arranged the retort so that the end of it projected into a bell jar *B* filled with air. The open end of the bell jar dipped into some mercury contained in the basin *C*, so that the air in the bell jar was trapped. He now heated the mercury in the retort and discovered that, as it burned, the volume of the air in the bell jar diminished. Other experiments proved that this diminution in volume was due to

the fact that the oxygen present in the air had combined with the metal in the retort, and that the metal had increased in weight by exactly the weight of the oxygen removed from the air.

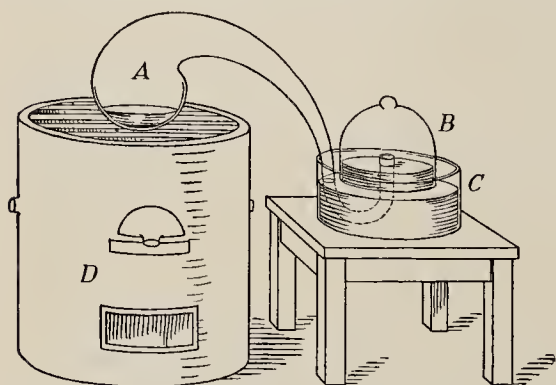


FIG. 11. Apparatus used by Lavoisier to prove that mercury absorbs oxygen during burning

**Rapidity (or speed) of oxidation.** It is a matter of common knowledge that the

same substance may burn with different degrees of rapidity, and it is important for us to know how the rapidity (or speed) of the oxidation can be increased or decreased. This question will be discussed in detail in a later chapter. For the present it is sufficient to state that a number of factors may affect this change, the most important of which are (1) *temperature*, (2) *the presence of a suitable catalytic agent*, and (3) *the quantity of oxygen that can be brought into contact with the substance undergoing combustion*.

For example, a log of wood burns slowly. Cut the log into pieces and the speed of combustion increases because more oxygen comes in contact with the wood. Split the pieces into fine splinters and the speed of combustion is still further increased. Grind the fine splinters into dust and float these in the air so that each little particle is surrounded by the oxygen

in the air, and combustion, if started, will take place so rapidly as to be nearly instantaneous, producing a violent explosion. In this way we account for the explosions that take place in flour mills and grain elevators, the air of which often contains large quantities of dust. Most of the explosions which occur in coal mines are due to the same cause.

**Importance of oxygen.** Oxygen is one of the most important of the elements. It is essential to all forms of life except some



FIG. 12. Sewage-disposal plant at Columbus, Ohio, in which the sewage is sprayed into the air to assist in the oxidation of the putrid matter

low species of plant life. In the presence of certain minute microorganisms, which in some way assist in the process, the oxygen in the air acts upon the dead products of animal and vegetable life and converts them into harmless substances. In this way it acts as a purifying agent. For example, in sewage-disposal plants, sewage is forced into the atmosphere in fine sprays (Fig. 12) so that the oxygen can come in contact with the putrid matter in the sewage, thus purifying the sewage and preventing it from becoming a menace to health.

The chief uses of pure oxygen are (1) for burning out the carbon which collects in the cylinders of gas engines and

(2) as a source of heat in the welding of metals (see oxy-acetylene blowpipe). Over one hundred tons of the element is used daily in the United States for these purposes. Small quantities of oxygen are also used in the treatment of certain diseases in which the patient is unable to inhale sufficient air to supply the necessary quantities of oxygen. Aviators are supplied with the pure gas for use at high altitudes. Oxygen is also used in the preparation of certain compounds.

**The definiteness of chemical processes.** Throughout this chapter attention has been directed repeatedly to the fact that chemical processes involve definite weights of matter. For example, the composition of a number of compounds has been expressed in exact percentages, since experiment has shown that these compounds always have precisely the composition stated, irrespective of the source from which they are obtained or the method by which they are prepared. After extensive investigation of a very large number of compounds, chemists have concluded that this *constancy of composition is a characteristic of every true compound*, and a statement of this characteristic is commonly called the *law of definite composition*.

In like manner, *the chemical changes which compounds undergo are always perfectly definite under stated conditions*. Thus, when potassium chlorate is heated, for every 100 g. decomposed there results 39.16 g. of oxygen and 60.84 g. of potassium chloride. When iron burns in oxygen, 100 g. of iron combines with 38.20 g. of oxygen to form 138.20 g. of oxide of iron. If less than 38.20 g. of oxygen is present, then a corresponding amount of iron will remain unchanged. On the other hand, if more than 38.20 g. of oxygen is present, then all the iron will be changed into the oxide, and the excess of oxygen will remain unaltered. The actual experiments which justify these conclusions will come before us from time to time as we proceed.

**Solution of problems.** These facts, that all compounds have a fixed composition and that chemical processes are definite, enable us to solve many chemical problems.



Thus, suppose we wish to know what weight of potassium chlorate is necessary for the preparation of 100 g. of oxygen. As already stated (p. 28), the composition of potassium chlorate as determined by experiment is as follows: potassium, 31.9 per cent; chlorine, 28.94 per cent; oxygen, 39.16 per cent. In other words, 100 g. of potassium chlorate contains 39.16 g. of oxygen. To prepare 1 g. of oxygen would require, therefore,  $100 \div 39.16$ , or 2.55 g., of potassium chlorate. To prepare 100 g. of oxygen, then, would require  $2.55 \times 100$ , or 255 g., of potassium chlorate.

It must be kept in mind that the composition of a compound is always expressed in *percentage by weight*. If we wish to calculate what weight of potassium chlorate is necessary for the preparation of, say, 100 *liters* of oxygen, it is first necessary to calculate the weight of the 100 liters of the gas. By referring to the Appendix it will be found that 1 liter of oxygen weighs 1.429 g.; hence 100 liters of oxygen weighs  $100 \times 1.429$ , or 142.9 g. It is then easily possible by the method described above to calculate the weight of potassium chlorate necessary to prepare the 142.9 g. of oxygen.

### EXERCISES

In all the problems in this text which involve volumes of gases, it is understood that, unless otherwise stated, the volumes referred to are those which the gas will occupy at a temperature of  $0^{\circ}$  and under a pressure of 1 atmosphere.

1. In Fig. 8 why does the water stay in the inverted cylinder? Why does the oxygen displace it? When a little oxygen has entered, why does not all the water run out?
2. Suggest a method for collecting a gas that is soluble in water.
3. Why is it that the discovery of oxygen is ordinarily attributed to Priestley, although others had obtained it before him?
4. Report brief accounts of the lives of Priestley, Scheele, and Lavoisier (consult encyclopedia).
5. Can combustion take place without the evolution of light?
6. Is the evolution of light always produced by combustion?
7. Suggest a reason why wood in the form of shavings burns more rapidly than the same wood in the form of a log.
8. Why do substances burn more rapidly in pure oxygen than in air?



9. For what purposes is oxygen used in repairing motor cars?

10. Suggest a reason why some metals tarnish on exposure to air, while others remain bright.

11. Consult the dictionary for the derivation and significance of the word *phlogiston*.

12. Why do some substances leave an ash on burning, while others do not?

13. (a) Why do various kinds of coal (chiefly carbon) differ in the amount of ash formed when they burn? (b) Which kind should you expect to liberate the most heat?

14. Why do some materials tend to undergo spontaneous combustion, so that they are considered bad insurance risks, while others do not?

15. Why blow a candle to extinguish a flame but blow a feebly burning stick of wood to make it burn better?

16. Calculate the weight in grams of each of the following compounds necessary for the preparation of 50 liters of oxygen: (a) mercuric oxide; (b) water; (c) potassium chlorate. *9.2-7*

17. Calculate the volume of oxygen that would be evolved on heating 10 g. of potassium chlorate; 10 g. of mercuric oxide. *15.2*

18. Assuming the cost of potassium chlorate and mercuric oxide to be respectively 70 cents and \$3.90 per kilogram, calculate the cost of materials necessary for the preparation of 50 liters of oxygen from each of the above compounds. *1.84*

19. 100 g. of potassium chlorate and 25 g. of manganese dioxide were heated in the preparation of oxygen (Fig. 8). Give the weight of each of the products left in the flask. *2.95*  
*5.84*

## CHAPTER IV

### HYDROGEN

**Introduction.** We have learned that water is a compound of oxygen and hydrogen. Having studied something of the properties of oxygen, we will now proceed with the study of hydrogen. These two elements, oxygen and hydrogen, are alike in many of their properties, but differ greatly in others. Thus, hydrogen is nearly sixteen times lighter than oxygen, and it is the only one of the gaseous elements that will burn in the air under ordinary conditions.

**Properties.** Like oxygen, hydrogen is a colorless, odorless, and tasteless gas. Its solubility in water is very small, being less than half that of oxygen. It is the lightest of all known substances, being 14.385 times lighter than air. One liter of the gas weighs only 0.08987 g. Soap bubbles filled with hydrogen rapidly rise in the air. The lightness of the element suggests its use as a material for inflating balloons, and it has been used extensively for this purpose, especially during the World War.

The English scientist Dewar was the first to obtain hydrogen in the liquid state. He cooled the gas to a temperature of  $-205^{\circ}$  by means of liquid air, and at the same time subjected it to a pressure of 180 atmospheres. It was obtained as a colorless, transparent liquid, boiling at  $-252.7^{\circ}$ . This is the lightest liquid known, having a density of but 0.07 at its boiling point. When liquid hydrogen is evaporated under very small pressure, solid hydrogen is obtained as a snowlike body melting at  $-259.1^{\circ}$ .

**Occurrence.** In the free state hydrogen is found in the atmosphere, but only in traces (about 1 volume in from

10,000 to 15,000 volumes of air). In the combined state it is widely distributed, being a constituent of water as well as of all living organisms and the products derived from them, such as starch and sugar. About 10 per cent of the human body is hydrogen. Combined with carbon, it forms the substances which constitute petroleum and natural gas. It is an interesting fact that while hydrogen in the free state occurs only in traces on the earth, it occurs in enormous quantities in the gaseous matter surrounding the sun and certain other stars.

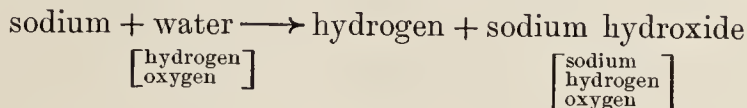
**Historical.** The element hydrogen was first clearly recognized as a distinct substance by the English investigator Cavendish, who in 1766 obtained it in a pure state and showed it to be different from the other inflammable airs, or gases, which had long been known. Because it had been found to be a constituent of water, Lavoisier gave it the name *hydrogen*, which means "water former."

**Preparation from water.** Since water contains hydrogen and is so abundant and inexpensive, it is but natural that we should try to obtain the element from this source. To do this we must separate it from the oxygen with which it is combined in water. Several ways of doing this are known, the most important of which are the following:

1. **By the electric current.** As has been indicated in Chapter II (p. 19), water is easily separated into its constituents, hydrogen and oxygen, by passing an electric current through it under certain conditions.

2. **By the action of certain metals.** When brought into contact with certain metals under appropriate conditions, water gives up a part or the whole of its hydrogen, the place of the hydrogen being taken by the metal. In the case of a few of the metals this change occurs at ordinary temperatures. Thus, if a bit of sodium is thrown on water, an action is seen to take place at once, sufficient heat being generated to melt the sodium, which runs about on the surface of the water. The

change which takes place consists in the displacement of one half of the hydrogen of the water by the sodium, and may be represented as follows:



The sodium hydroxide formed is a white solid which remains dissolved in the excess of undecomposed water and may be obtained by evaporating the solution to dryness. The hydrogen is evolved as a gas and may be collected by suitable means.

**Laboratory apparatus.** A simple form of apparatus used in preparing hydrogen by the action of sodium on water is represented in Fig. 13. Since the sodium is lighter than water, it is kept under the water by pushing a pellet of the metal into the end of a short piece of glass tubing, the other end of which has been sealed. The tube containing the sodium is then dropped into a vessel of water. Hydrogen is at once evolved and is collected by bringing over it a bottle or cylinder filled with water, as shown in the figure.

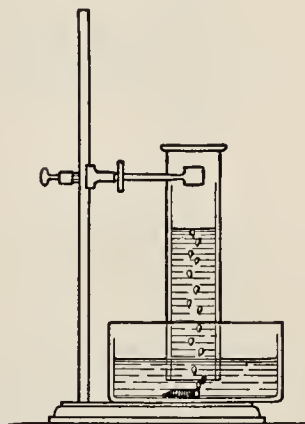
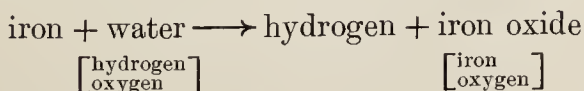


FIG. 13. The preparation of hydrogen by the action of sodium on water

Other metals, such as magnesium and iron, decompose water rapidly but only at higher temperatures. When steam is passed over hot iron, for example, the iron combines with the oxygen of the steam, setting free all the hydrogen. Experiments show that the change may be represented as follows:



The iron oxide formed is a reddish-black compound identical with that obtained by the combustion of iron in oxygen.

**Preparation of hydrogen from iron and steam.** The apparatus used in the preparation of hydrogen from iron and steam is shown in Fig. 14. A porcelain or iron tube *A*, about 50 cm. in length and 2 cm. or 3 cm. in diameter, is loosely filled with fine iron wire or tacks and connected as shown in the figure. The tube is heated, slowly at first, until the iron is red-hot. Steam is then conducted

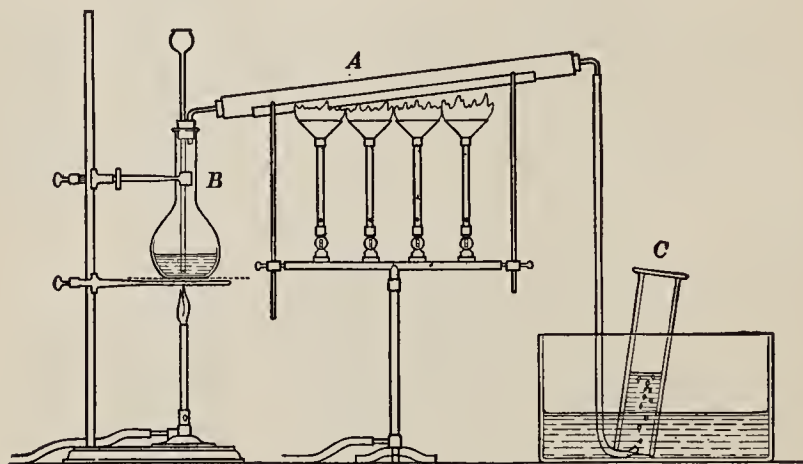


FIG. 14. The preparation of hydrogen by the action of iron on steam

through the tube by boiling the water in the flask *B*. The hot iron combines with the oxygen in the steam, setting free the hydrogen, which is collected over water in *C*.

### 3. *By the action of acids on metals (usual laboratory method).*

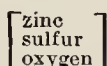
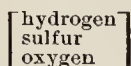
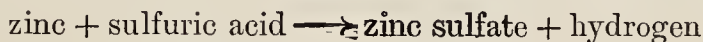
The *acids* constitute a very important class of compounds and we shall have much to do with them as we proceed with our study. For the present it is only necessary to say that all acids consist of certain compounds of hydrogen dissolved in water, and that when certain metals are brought in contact with them the metal takes the place of the hydrogen of the acid. The hydrogen is thus liberated in a free state and is easily collected over water, as in the case of oxygen.

It has been found most convenient and economical in preparing hydrogen by this method to use either *zinc* or *iron* as the metal and either *hydrochloric acid* or *sulfuric acid* as the



acid. Hydrochloric acid is an aqueous solution of a gaseous compound known as *hydrogen chloride* (which consists of 2.77 per cent of hydrogen and 97.23 per cent of chlorine), while sulfuric acid is an aqueous solution of an oily liquid known as *hydrogen sulfate* (which consists of 2.05 per cent of hydrogen, 32.70 per cent of sulfur, and 65.25 per cent of oxygen).

The changes taking place in the preparation of hydrogen from zinc and sulfuric acid may be represented as follows:



In other words, the zinc takes the place of the hydrogen in sulfuric acid. The resulting compound contains zinc, sulfur, and oxygen and is known as *zinc sulfate*. This remains in solution after the action is over. It may be obtained in the form of a white solid by evaporating the liquid left after the action has ceased.

When iron and hydrochloric acid are used in the preparation

of hydrogen, the reaction may be represented as follows:

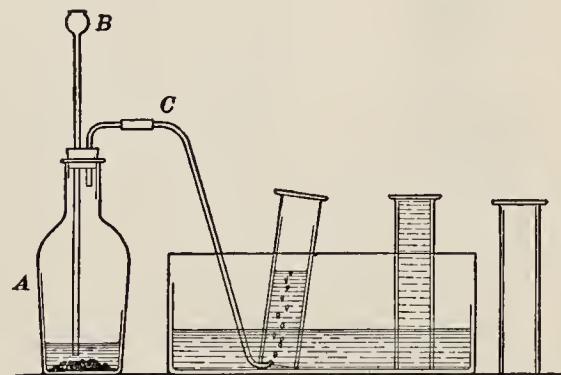
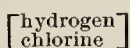
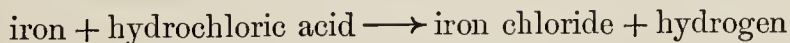


FIG. 15. The preparation of hydrogen by the action of metals on acids

**Laboratory apparatus.** A convenient form of apparatus for preparing hydrogen by the action of metals upon acids is shown in Fig. 15. The metal is placed in flask *A*, which is fitted with a stopper and connected with tubes, as shown in the figure. The acid, properly diluted with water, is added a little at a time

through the funnel tube *B*. The liberated hydrogen escapes through *C* and is collected in receivers, as shown in the figure. The hydrogen which first escapes through the exit tube is mixed with the air originally present in flask *A*. *Such a mixture of hydrogen and air is violently explosive when brought in contact with a flame.* Therefore one must keep all flames away from the apparatus. Moreover, one should not collect the hydrogen until an amount of it has been generated sufficient to displace all the air previously contained in the flask.

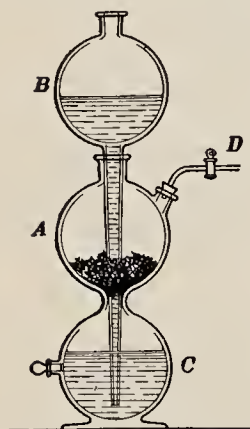


FIG. 16. A Kipp generator for preparing hydrogen

A more convenient form of apparatus to use is that shown in Fig. 16. It is known as a *Kipp generator*, and it has the advantage of being automatic in its action. The metal is placed in *A*, and the acid is poured into *B*. When the stopcock *D* is opened, the acid runs down into *C* and up into *A*, where it comes in contact with the metal. The hydrogen generated escapes through *D*. If now the stopcock is closed, the hydrogen, being unable to escape through the tube, pushes the acid away from the metal in *A* down into *C* and up into *B*, so that the action ceases.

**Commercial preparation of hydrogen.** A number of different methods are employed for preparing hydrogen when large quantities are desired for commercial purposes. In some cases it is liberated from water either by the electric current or by passing steam over heated iron. Sometimes it is obtained from sulfuric acid by the action of iron, or from sodium hydroxide (p. 43) by the action of the element silicon. It is also prepared by the action of heated carbon on steam, as well as by the decomposition of certain compounds of carbon and hydrogen, such as the common acetylene used for welding metals. These methods will be referred to in later chapters.

**Chemical conduct.** At ordinary temperatures hydrogen is not an active element. Under suitable conditions, however, it combines directly with many of the elements and forms

important compounds collectively known as *hydrides*. Thus, with nitrogen it forms the well-known gas *ammonia*, the aqueous solution of which we use in our homes under the name *aqua ammonia*, or ammonia water. With sulfur it forms the foul-smelling gas *hydrogen sulfide*. When mixed with the gaseous element chlorine (Chapter XV) in the dark, no action takes place; but if the mixture is heated, or if it is exposed to the sunlight, the hydrogen and the chlorine in the mixture combine with explosive violence, forming the compound *hydrogen chloride*, whose solution in water constitutes ordinary hydrochloric acid (p. 45). Similarly, hydrogen and oxygen (or air, which contains oxygen) may be mixed together at ordinary temperatures without any apparent action. If the mixture is heated to about  $800^{\circ}$ , however, or if a flame is brought in contact with the mixture, the two gases combine with explosive violence, forming water, which is, of course, in the form of steam at the temperature of the explosion.

Mixtures of pure hydrogen and pure oxygen explode with such violence that they should not be made and exploded *except in small quantities and by experienced workers*. That a mixture of these two gases is explosive may be shown with perfect safety by substituting air for pure oxygen. Since air is only about one fifth oxygen, the remainder being composed of inert gases (principally nitrogen), the force of the explosion is greatly diminished. The experiment is conducted in the following way:

**Laboratory experiment.** A cork through which passes a short glass tube about 1 cm. in diameter is fitted air-tight into the tubule of a bell jar (Fig. 17) of 2 or 3 liters' capacity. (A thick glass bottle with the bottom removed may be used.) The tube is closed with a small rubber stopper and the bell jar filled with hydrogen, the gas being collected over water. When entirely filled with the gas the jar is removed from the water and supported by blocks of wood in order to leave the bottom open, as shown in Fig. 17. The stopper is now removed from the tube in the cork. On account of its lightness, the hydrogen escapes from the tube and should be

at once lighted. As it escapes, the air is drawn in at the bottom of the jar and mixes with the remaining portion of the hydrogen. A mixture of the two soon forms, and when this reaches the flame a loud explosion results. The explosion is not dangerous, since the bottom of the jar is open, thus leaving room for the expansion of the hot steam formed.

The explosion is due to the fact that the large amount of heat generated by the union of the hydrogen and oxygen raises the temperature of the steam formed by their union to a high degree, and this is accompanied by a corresponding increase in the volume of the steam. The result is that the volume of the hot steam is much greater than the combined volumes of hydrogen and oxygen which have united to form the steam, and it is this sudden increase in the volume of the gases involved in the reaction which constitutes the explosion.

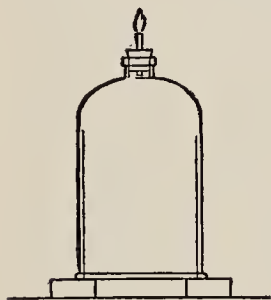


FIG. 17. Exploding a mixture of hydrogen and oxygen

### Burning hydrogen in oxygen or in air.

While a mixture of hydrogen and oxygen explodes with great violence when ignited, nevertheless, under appropriate conditions, the two gases may be made to unite quietly and with perfect safety. The union is attended by the production of a flame, and we say that the hydrogen burns in oxygen or in the air which contains the oxygen. The experiment is carried out as follows:

**Experimental apparatus.** The hydrogen is generated in the bottle *A* (Fig. 18), is dried by conducting it through the tube *B* filled with some substance (usually calcium chloride) which has a great attraction for moisture, and escapes through the tube *C*, the end of which is drawn out to a jet. *When all the air has been expelled from the apparatus, the hydrogen may be ignited by bringing a flame for an instant to the end of the exit tube C.* The hydrogen then burns quietly, since only the small amount of it which escapes from the jet can come in contact with the oxygen of the air at any one time. By holding a cold, dry bell jar or bottle over the flame in the manner shown in the figure the steam



formed by the combustion of the hydrogen is condensed, water collecting in drops on the sides of the jar.

**Temperature at which hydrogen combines with oxygen.** The union of hydrogen and oxygen probably takes place at ordinary temperatures, but the speed of the reaction is so slow that no combination can be detected even after long intervals of time. As the temperature is raised the speed increases. Thus, Meyer and Raun found that the two gases, when mixed in the proportion of two volumes of hydrogen to one volume of oxygen and heated to  $100^{\circ}$  for 218

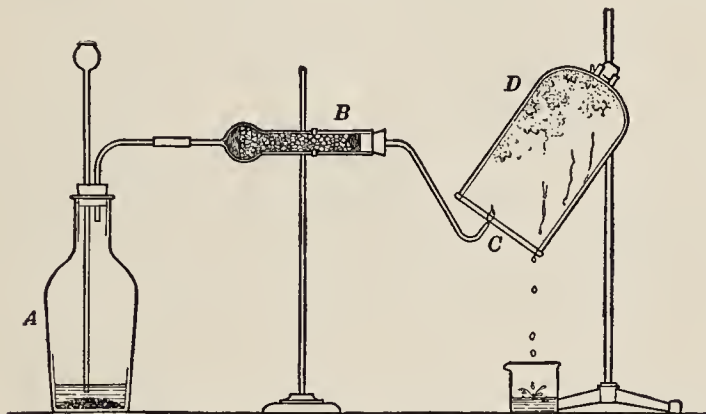


FIG. 18. Burning hydrogen and collecting the product of its combustion

days, showed no appreciable combination. When heated to  $300^{\circ}$  for 65 days it was found that, in different trials, from 0.4 per cent to 9.5 per cent of the mixture had combined. At  $500^{\circ}$  the change is still more rapid, but requires several hours for completion. At a temperature roughly approximating  $800^{\circ}$  the union of the two takes place with explosive violence. The temperature at which this instantaneous combination takes place is modified by very slight changes in the conditions, due to the catalytic effect of foreign substances, such as moisture and the materials of which the tube containing the gases is made. Certain catalyzers, such as finely divided platinum, bring about almost instantaneous combination at ordinary temperatures.

**Proportions in which hydrogen and oxygen combine to form water.** Experiments show that when hydrogen and oxygen combine to form water, 1 part by weight of hydrogen always



combines with 7.94 parts by weight of oxygen; or, expressed in volumes, 2 volumes of hydrogen combine with 1 volume of oxygen. Moreover, for each gram of hydrogen entering into combination with oxygen there is liberated 28,933 cal. of heat if the water produced remains in the state of vapor (steam), or 34,221 cal. if the resulting vapor is condensed to the liquid state.



FIG. 19. Flame of a candle extinguished by hydrogen

**Hydrogen does not support combustion.** While hydrogen is readily combustible, it is not a good supporter of combustion; in other words, most substances will not burn in it. This may be shown by bringing a lighted candle supported by a stiff wire into a bottle or cylinder of the pure gas, as shown in Fig. 19. The hydrogen is ignited by the flame of the candle and burns at the mouth of the cylinder, where it comes in contact with the oxygen in the air. When the candle is thrust up into the gas, its flame is extinguished. If slowly withdrawn, the candle is relighted as it passes through the layer of burning hydrogen.

**Reduction; reducing agent.** On account of its tendency to combine with oxygen, hydrogen has the power of abstracting it from many of its compounds.

Thus, if a stream of hydrogen generated in *A* (Fig. 20) and dried by passing through the tube *B* (filled with calcium chloride) is conducted through the tube *C*, which

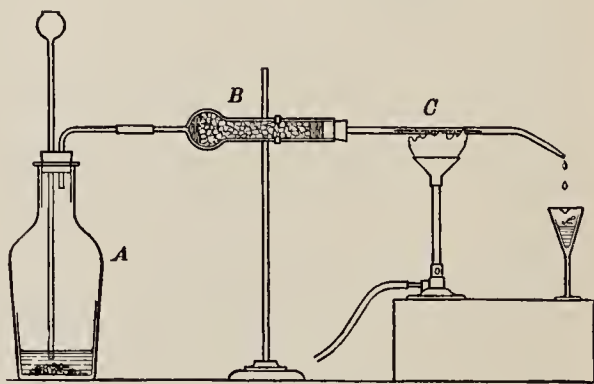
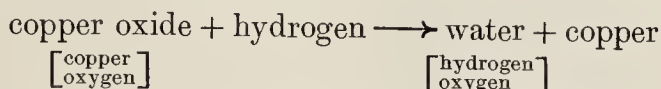
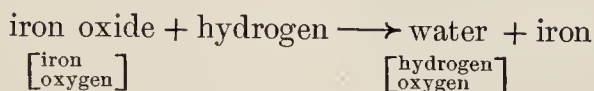


FIG. 20. The reduction of hot copper oxide by a stream of hydrogen

contains some copper oxide heated to a moderate temperature, the hydrogen abstracts the oxygen from the copper oxide. The change may be represented as follows :



The oxides of most of the metals act in a similar way. Thus, when hydrogen is passed over hot iron oxide, water and iron are formed :



In these reactions the oxide of the metal is said to undergo *reduction*. *Reduction may be defined, therefore, as the process of removing oxygen from a compound.* An element, such as hydrogen, which has a strong affinity for oxygen, and which may be used for removing oxygen from a compound, is termed a *reducing agent*.

**Relation of oxidation and reduction.** It is evident from the statements concerning oxidation and reduction that the two processes are just the opposite of each other. The one process consists in the addition of oxygen to an element or compound, while the other consists in the removal of oxygen from a compound. Moreover, it usually happens that when one substance is oxidized, some other substance is reduced. Thus, when hydrogen is passed over hot copper oxide (Fig. 20), the hydrogen is oxidized, while the copper oxide is reduced. It will be pointed out later that the terms *oxidation* and *reduction* are sometimes used with broader meanings than those just given.

**The oxyhydrogen blowpipe.** This is a form of apparatus used for burning hydrogen in pure oxygen. It was devised and first used by an American scientist, Robert Hare (Fig. 21), in the year 1801, in his laboratory in Philadelphia. As has been previously stated, the flame produced by the combustion of hydrogen in the air is very hot. It is evident that if pure oxygen is substituted for air, the temperature reached will be much higher, since there are no

inert gases to absorb the heat. The oxyhydrogen blowpipe, used to effect this combination, consists of a small tube placed within a larger one, as shown in Fig. 22.

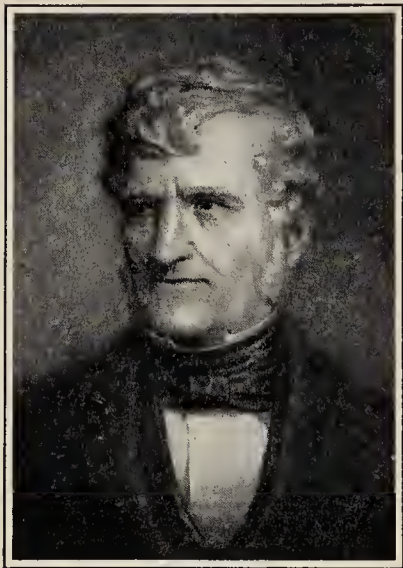


FIG. 21. Robert Hare (1781–1858)

An early American chemist; the inventor of many ingenious laboratory appliances, including the oxyhydrogen blowpipe

The hydrogen, stored under pressure, usually in steel cylinders, is first passed through the outer tube *H* (Fig. 22) and ignited at the open end of the tube *A*. The oxygen from a similar cylinder is then conducted through the inner tube *O* and mixes with the hydrogen at the end of the tube. In order to produce the maximum heat the hydrogen and oxygen must be admitted to the blowpipe in the exact proportion in which they combine; namely, 2 volumes of hydrogen to 1 of oxygen, or, by weight, 1 part of hydrogen to 7.94 parts of oxygen. The intensity of the heat may be shown by bringing into the flame pieces of metal such as iron wire or zinc. These burn with great brilliancy.

Even platinum, which has a melting point of  $1755^{\circ}$ , may be melted by the heat of the flame.

**The blast lamp.** A similar form of apparatus is used in the laboratory as a source of heat under the name *blast lamp* (Fig. 23). This differs from the oxyhydrogen blowpipe only in the size of the tubes. In place of the hydrogen and oxygen the more accessible coal gas (or natural gas) and air are used.

Coal gas and natural gas are composed largely of a mixture of gaseous compounds of carbon and hydrogen (Chapter XXVII). While

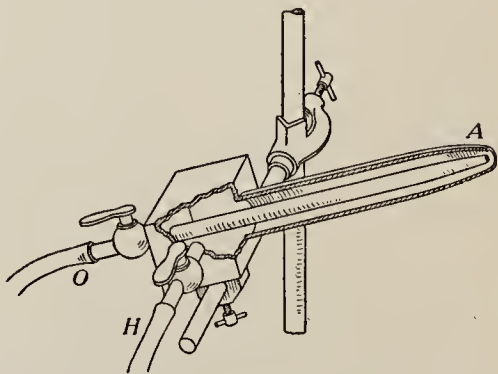


FIG. 22. The oxyhydrogen blowpipe

the temperature of the flame is not so high as that of the oxyhydrogen blowpipe, it nevertheless suffices for most chemical operations.

**Exothermic and endothermic reactions.** We have seen that in certain reactions a large amount of heat is given off. Examples of such reactions are the combustion of hydrogen in oxygen and the combustion of coal in air. All such reactions are said to be *exothermic*. In other reactions heat is continuously absorbed and so must be applied in order that the reaction may continue. Such reactions are termed *endothermic*. The decomposition of mercuric oxide (p. 28) is an example of an endothermic reaction.

**Uses of hydrogen.** Hydrogen is used for inflating balloons and dirigible airships, such as the Zeppelins so largely used in the World War. The fact that it is combustible makes it a dangerous gas to use for this purpose, so that it is gradually being replaced by the noncombustible gas helium, as will be described in a later chapter. The chief use of hydrogen in time of peace is for the refining of certain oils, such as cottonseed oil, whereby these oils not only are purified but are transformed into solid or semisolid fats which may be used in cooking and in making soaps. Large quantities of hydrogen are used in Germany in the preparation of ammonia, as will be explained in a later chapter; smaller quantities are used in the United States for the same purpose.

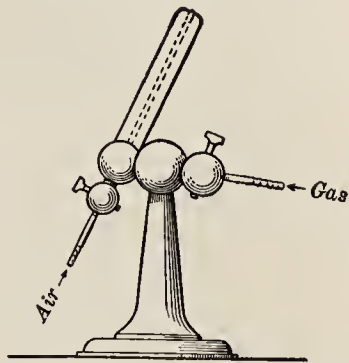


FIG. 23. The ordinary laboratory blast lamp

#### EXERCISES

1. Report the important events in the life of Cavendish (consult encyclopedia).
2. Will a definite weight of iron decompose an unlimited weight of steam?
3. Calculate the relative weight of hydrogen and oxygen (see weights of 1 liter of different gases, in Appendix).



4. Why is oxygen passed through the inner tube of the oxyhydrogen blowpipe rather than the outer?

5. Water dissolves sugar, and sulfuric acid dissolves zinc. In what respect do the two processes differ from each other?

6. In the experiment illustrated by Fig. 19, will the flame remain at the mouth of the cylinder?

7. Distinguish clearly between the following terms: *oxidation*, *reduction*, *combustion*, and *kindling temperature*.

8. Is oxidation always accompanied by reduction?

9. In the experiment illustrated by Fig. 18, why dry the hydrogen before burning it?

10. Suggest a way of determining the weight of the water formed in the reaction in the experiment illustrated by Fig. 20.

11. If hydrogen and oxygen unite in the ratio of 1 to 7.94 by weight, in what ratio do they unite by volume?

12. (a) How many calories of heat are evolved in the combustion of 100 liters of hydrogen to form water? (b) How many grams of water are formed?

13. How many grams of hydrogen can be obtained from 100 g. of hydrogen sulfate? What volume would this weight of hydrogen occupy?

14. A gas tank holds 250 liters of hydrogen. (a) What is the weight of this volume of hydrogen? (b) What weight of water would have to be decomposed by electricity in order to prepare this volume of hydrogen? (c) What volume of oxygen would be liberated in the process?

15. 10 g. of water is boiled and the steam passed over heated iron (Fig. 14). (a) What weight of hydrogen will be liberated? (b) What volume will the hydrogen occupy? (c) What change will the iron undergo?

16. Suppose you had 1 kg. of water with which to prepare hydrogen. Which of the following methods would yield the largest amount of hydrogen: (a) decomposition by the electric current; (b) decomposition by iron; (c) decomposition by sodium?

17. In passing hydrogen over heated copper oxide (Fig. 20) 22.5 g. of water was formed. What is the loss in the weight of the copper oxide?

18. Suppose that 10 liters of hydrogen and 15 liters of oxygen were mixed together and ignited. What would be the products of the reaction? Calculate the weight of each.

19. Calculate the volume of hydrogen that could be obtained from each of the following: (a) 100 g. of hydrogen sulfate; (b) 100 g. of hydrogen chloride; (c) 100 g. of water.



## CHAPTER V

### THE GAS LAWS; THE KINETIC THEORY; AVOGADRO'S PRINCIPLE

**Introduction.** It will be remembered that in describing the properties of oxygen and hydrogen the weight of a liter of each gas was given. A moment's reflection will make it clear that these weights can be correct only under certain conditions, for it is a familiar fact that the volume of a given weight of a gas varies both with changes in pressure and with changes in temperature.

**Variation of volume with pressure: law of Boyle.** That the volume occupied by a given weight of gas can be altered by changing the pressure is familiar to everyone who has pumped air into the tire of a bicycle or automobile. As early as 1660 Robert Boyle (Fig. 24) showed that the following statement, known as *Boyle's law*, correctly expresses the relation between volume and pressure. *The volume occupied by a given weight of a gas varies inversely as the pressure to which it is subjected, provided the temperature of the gas remains constant.* For example, if a given weight of a gas occupies a volume of 1000 cc. when subjected to a certain pressure, it will occupy a volume of 500 cc. if the pressure is doubled, or of 2000 cc. if the pressure is diminished one half. This means that for a given weight of gas the product of the pressure by the volume will remain constant, no matter how either one may be altered. Designating the pressure and volume under one set of conditions by  $P$  and  $V$ , and under a different set by  $P'$  and  $V'$ , Boyle's law may be stated thus:

$$PV = P'V'$$



FIG. 24. Robert Boyle  
(1627-1691)

Distinguished Irish scientist. The first clearly to define an element. The first to define a compound as formed of two constituents. Helped to perfect the air pump. Demonstrated that sound cannot pass through a vacuum. Invented the term *chemical analysis*. Chiefly remembered for his work on gases and his formulation of Boyle's law. Author of a famous book entitled "The Sceptical Chymist"

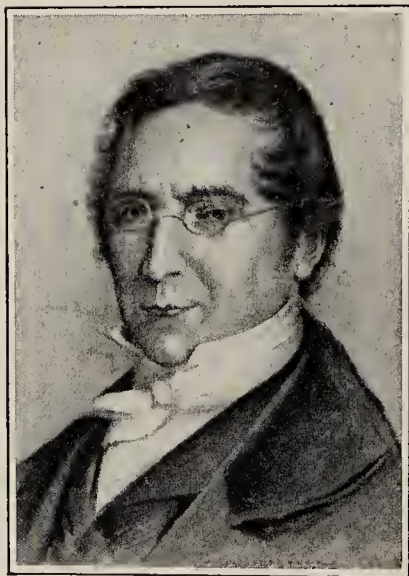


FIG. 25. Joseph Louis Gay-Lussac (1778-1850)

Distinguished French scientist. Formulated the law which states the rate at which all gases expand when heated, and more accurately than either Charles or Dalton, who formulated the same law about the same time (1801). Determined accurately the ratio by volume in which oxygen combines with hydrogen, as well as the combining ratio of many other pairs of gases. Investigated the cyanides and the compounds of iodine. One of the great teachers of his generation

FIG. 26. Ira Remsen  
(1846-1927)

For many years director of chemical research at the Johns Hopkins University and later president of that institution; known equally well as a great chemist, an inspiring teacher, and an educational leader; editor of an important chemical journal and the author of an important series of books; president of the American Chemical Society (1902); member and officer in many of the important scientific societies of this country as well as foreign member of many European societies

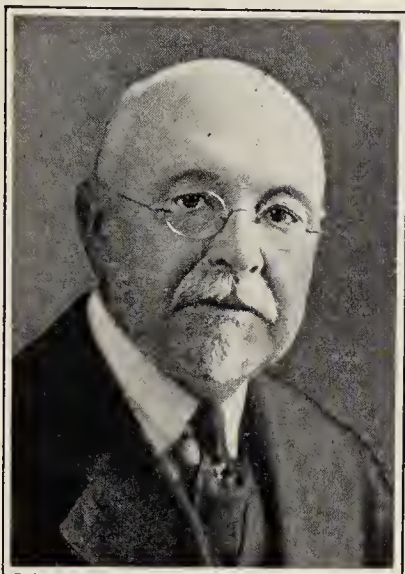
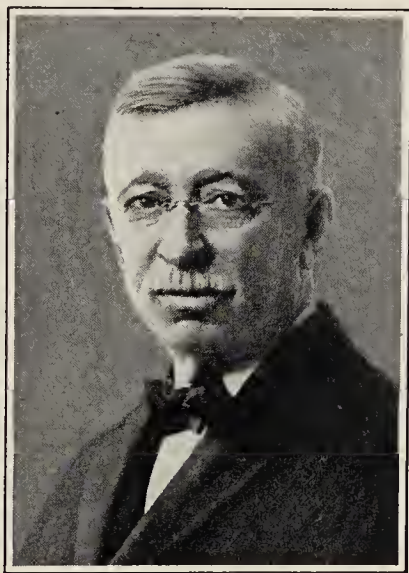


FIG. 27. Edgar Fahs Smith  
(1856-1928)

For many years director of chemical research at the University of Pennsylvania and later provost of that institution; noted for his contributions to electrochemistry and to our knowledge of the rarer elements; a writer of fascinating interest on the early history of chemistry in the United States; president of the American Chemical Society (1895, 1921, and 1922); member and officer in many scientific societies in this country and abroad



**Standard pressure.** For practical purposes we must choose some standard pressure to which all gas volumes may be referred. This is most conveniently chosen as the average pressure of the atmosphere at sea level. This is equal to 1033 g. per square centimeter. In place of expressing the pressure in this way it is much more convenient to express it in terms of the height of the column of mercury which the pressure of the atmosphere will sustain. Expressed in this way the standard pressure is equal to that exerted by a column of mercury 760 mm. in height, this being the average height of the barometer at sea level.

**Illustration of the law of Boyle.** The following problem will not only make the meaning of the law clear but will also show how the law enables us to calculate the changes in the volume of a gas due to changes in pressure :

A gas measured under a pressure of 720 mm. had a volume of 620 cc. What volume will this gas occupy under standard pressure, 760 mm., the temperature remaining constant ?

According to Boyle's law  $PV = P'V'$ . Substituting the values that are given in the problem, we have  $760 \times V = 720 \times 620$ , or  $V = 587.4$  cc.

**Variation of volume with temperature.** If the pressure is held constant, all gases expand when the temperature is raised, and contract when it is lowered, and it is a remarkable fact that the volumes of all gases change to the same extent for a given variation in the temperature. Let us suppose that the volume of a gas has been measured at zero on the centigrade scale. Experiment has shown that a rise of one degree causes an expansion of  $\frac{1}{273}$  of this volume ; a rise of five degrees, an expansion of  $\frac{5}{273}$ . If we take 273 cc. of this gas at zero, the volume at  $1^\circ$  above will be 274 cc. ; at  $1^\circ$  below it will be 272 cc. ; and at  $5^\circ$  below it will be 268 cc. At the same rate of contraction the volume will be 1 cc. at  $-272^\circ$ , and at  $-273^\circ$  it will be zero. Of course this cannot really happen, and experiment shows that *before this temperature is reached,*



*all gases have changed into liquids or solids.* Helium, the most difficult gas to liquefy, passes into a liquid at  $-268.7^{\circ}$ .

**The absolute scale.** For many purposes it has been found convenient to use a new scale of temperature known as the *absolute scale*; on this scale the divisions are of the same size as those on the centigrade scale, but the zero point is the same as  $-273^{\circ}$  on the centigrade scale; that is, the temperature at which the volume of any gas would apparently become zero (see preceding paragraph). The  $0^{\circ}$  on the centigrade scale would then be  $273^{\circ}$  on the absolute scale. On such a scale all temperatures are above the zero point. To convert readings on the centigrade scale to the corresponding ones on the absolute it is only necessary to add 273. Thus,  $20^{\circ}\text{C.} = 20 + 273^{\circ}$ , or  $293^{\circ}\text{A.}$ , while  $-20^{\circ} = -20 + 273$ , or  $253^{\circ}\text{A.}$  Fig. 28 gives a comparison of the centigrade and absolute scales at a number of temperatures.

**The law of Gay-Lussac (or of Charles).** A general statement can now be made in regard to the effect of temperature on the volume of a gas: *The volumes occupied by a given weight of a gas at different temperatures are proportional to the absolute temperatures, provided the pressure remains constant.* If  $V$  and  $V'$  are the volumes at the temperatures  $T$  and  $T'$ , then

$$V : V' = T : T', \text{ or } V = \frac{V'T}{T'}$$

The above generalization is called the law of Gay-Lussac (Fig. 25) or of Charles, and was formulated in 1801.

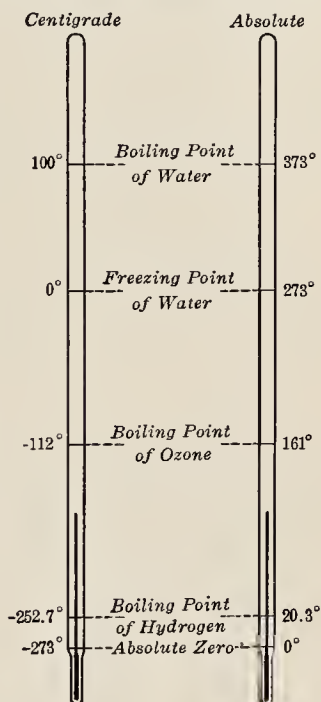


FIG. 28. Comparison of the centigrade with the absolute scale of temperature



**Illustration of the law of Gay-Lussac.** The following problem will make clear the meaning of the law. The volume of a certain gas measured at a temperature of  $70^{\circ}$  is 650 cc. What will be its volume at  $10^{\circ}$ ?

First reduce the centigrade readings to absolute:

$$70^{\circ} \text{ C.} = 70 + 273 = 343^{\circ} \text{ A.}; \quad 10^{\circ} \text{ C.} = 10 + 273 = 283^{\circ} \text{ A.}$$

Now, substituting the appropriate values in the equation on page 57, we have

$$V = \frac{650 \times 283}{343}; \text{ or } V = 536.3 \text{ cc.}$$

**Variations in volume due to changes both in pressure and in temperature.** In case both pressure and temperature change, then the correction may be made for each in succession, as illustrated in the following problem:

**Problem.** A certain weight of gas measured 500 cc. at a temperature of  $100^{\circ}$  when subjected to a pressure of 760 mm. Calculate the volume which this gas will occupy at a temperature of  $50^{\circ}$  and a pressure of 740 mm.

First make the correction for pressure:

$$PV = P'V'$$

$$740 \times V = 760 \times 500; \text{ or } V = 513.5 \text{ cc.}$$

Next make the correction for temperature:

$$V = \frac{V'T'}{T'}, \text{ or } V = \frac{513.5 \times 323}{373}; \text{ or } V = 444.6 \text{ cc.}$$

**Standard conditions.** Since the volume of a gas varies with both temperature and pressure, it is essential that we select both a *standard temperature* and a *standard pressure* to which we shall agree to refer all gas volumes. We have already noted that the *standard pressure adopted is that exerted by a column of mercury 760 mm. in height. As a standard temperature, the temperature of melting ice is chosen.* This is  $0^{\circ}$  centigrade or  $273^{\circ}$  absolute. Whenever the volume of a gas is given, it is always assumed, unless otherwise specified, that the volume is that occupied by the gas under standard conditions.

**Standard conditions and laboratory conditions.** The conditions of temperature and pressure which prevail in the laboratory are never the standard conditions. Knowing the volume of a gas under laboratory conditions, however, it is a simple matter to calculate the volume which the gas will occupy under standard conditions. The following problem will illustrate the method:

**Problem.** A gas measured 300 cc. under a pressure of 740 mm. and a temperature of  $25^{\circ}$  (or  $298^{\circ}$  A.). What will its volume be under standard conditions ( $0^{\circ}$  and 760 mm. pressure)?

First find the change in volume due to change in pressure:

$$300 \times 740 = 760 \times V; \text{ or } V = 292 \text{ cc.}$$

Next make the correction for temperature:

$$V = \frac{292 \times 273}{298}; \text{ or } V = 267.5 \text{ cc.}$$

**The relation of pressure to the absolute temperature.** We have seen that the volume of a gas varies with the pressure, and also with the absolute temperature. If the volume of the gas remains constant, then, *the pressure will vary directly with the absolute temperature*; that is,

$$P : P' :: T : T'.$$

**General formula for solving gas problems.** The relations between volume, pressure, and temperature as expressed in the laws stated earlier in this chapter may all be combined in the form of the equation

$$\frac{VP}{T} = \frac{V'P'}{T'}$$

The student may find it convenient to use this equation in solving the gas problems, since it is applicable in all cases. If the problem deals only with changes in volume due to changes of pressure, simply drop the terms  $T$  and  $T'$  and the equation becomes  $VP = V'P'$ . If the problem involves the changes in volume due only to change in temperature, then omit the factors  $P$  and  $P'$  and the equation becomes  $\frac{V}{T} = \frac{V'}{T'}$ . Again, if the problem has to do

with changes in pressure due to change in temperature, then omit the factors  $V$  and  $V'$  and the equation becomes  $\frac{P}{T} = \frac{P'}{T'}$ . Finally, if the problem deals with changes in volume due to changes in both pressure and temperature, then the complete formula  $\frac{VP}{T} = \frac{V'P'}{T'}$  is applicable.

**Vapor pressure of water.** It is well known to all of us that water exposed to the air in an open vessel slowly disappears; we say that the water evaporates. If we partially fill a flask with water and stopper the flask, a portion of the water evaporates as before, but the process soon ceases. At a given temperature there is a definite limit to the volume of water vapor which a definite volume of air can hold, and when this has been reached the air is said to be *saturated* with the water vapor. This vapor exerts a pressure, definite for any given temperature, upon the surface of the water, as well as on the sides of the flask. This pressure is known as the pressure due to the vapor of water, or, more briefly, the *vapor pressure of water*. The value of this pressure at different temperatures is given in the Appendix, expressed in terms of barometric pressure (millimeters of mercury). Every liquid possesses a definite vapor pressure at any given temperature, although the magnitude of the pressure varies widely with the liquid. Thus, the vapor pressure of water is relatively great, while that of mercury at ordinary temperature is very small. Even solids are known to possess a vapor pressure, although in many cases we have no instruments sufficiently delicate to detect it.

**Evaporation a continuous process.** When some water is placed in a flask and the flask is stoppered, a small amount of water evaporates as stated above, and then the process seems to cease. As a matter of fact the evaporation continues, but after the air in the flask has become saturated with vapor, the amount of vapor escaping from the liquid into the air in the flask is exactly equal to

the amount returning from the air to the liquid. Hence the volume of the liquid and the percentage of the vapor in the air remain unchanged.

**Determination of vapor pressure.** The pressure of the vapor of a liquid at any temperature may be determined experimentally in the following way: Two long barometer tubes are filled with mercury and inverted in an open vessel of the same liquid (Fig. 29). A few drops of the liquid to be examined are introduced under the open end of one of the tubes, the liquid so introduced immediately rising to the top of the mercury column. Evaporation at once takes place, and because of the pressure of the gas so formed the mercury column falls to some extent. When equilibrium is reached, the difference in level of the mercury in the two tubes, included between the dotted lines *A* and *B* in the figure, will correspond to the pressure of the vapor of the liquid expressed in millimeters of mercury. The tubes may be surrounded by jackets through which heated liquids are circulated, so that any desired temperature may be secured.

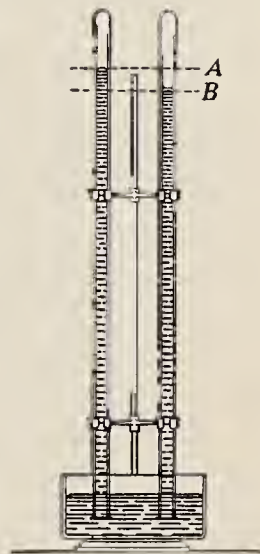


FIG. 29. Method of measuring the vapor pressure of a liquid

**Pressures exerted by mixtures of gases ; Dalton's law of partial pressures.** The gas laws that we have studied hold good for a mixture of gases as well as for a single gas, provided the gases composing the mixture do not react chemically upon each other. Thus, suppose that 50 cc. of hydrogen and 50 cc. of oxygen are mixed together. The resulting mixture will have a volume of 100 cc. and each of the gases will be distributed uniformly throughout this space. Moreover, the pressure exerted by this gaseous mixture is equal to the sum of the pressures which the oxygen and hydrogen would exert if each separately occupied the entire volume (100 cc.). This general principle is known as *Dalton's law of partial pressure* and may be stated as follows: *The total pressure exerted by*

*a mixture of gases is equal to the sum of the pressures which the different gases would exert if each separately occupied a volume equal to the whole space filled by the mixture of gases.*

**The measurement of the volume of gases collected over water.** In the laboratory, gases are frequently collected over water. In such cases, if we know the volume of the gas and the laboratory conditions of temperature and pressure, it is

easily possible to calculate the volume which the dry gas would occupy under standard conditions; knowing this we can calculate the weight of the gas (the weights of 1 liter of each of the common gases, measured under standard conditions, are given in the Appendix).

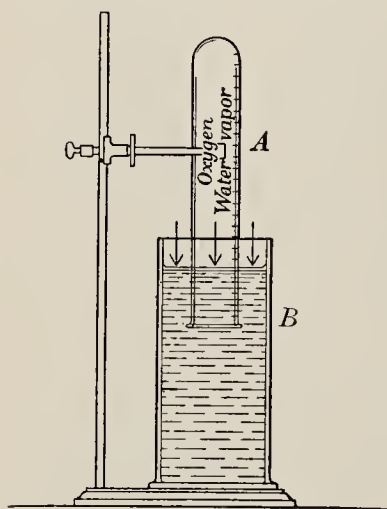


FIG. 30. Measuring the volume of a gas collected over a liquid

this oxygen would occupy under standard conditions. The tube *A* is first lowered in the water until the level of the liquid within and without the tube is the same. The volume of the gas in the tube is then read off on the scale on the tube. Now when the level of the liquid within and without the tube is the same, the pressure exerted by the atmosphere (as indicated by the barometer reading) upon the surface of the water in the open vessel *B*, and tending to force the liquid up into the tube *A*, is in equilibrium with the pressure of the gas in the tube, which tends to prevent the water from rising. The gas in the tube, however, is not pure oxygen but a mixture of oxygen and water vapor. Moreover, the pressure exerted by the gas in the tube is equal to the sum of the partial pressures of the water vapor and the oxygen (Dalton's law

**Illustration.** For example, let us suppose that we have a graduated tube *A* (Fig. 30) entirely filled with water, and that we have collected in it the oxygen evolved on heating a certain weight of potassium chlorate. We wish now to determine the volume which



of partial pressure). If now we subtract from the atmospheric pressure the pressure exerted by the aqueous vapor (given in the Appendix), the difference will be the pressure at which the oxygen in the tube would occupy the entire space filled with the gas. The correction for change in volume and temperature can then be made just as in the case of pure gases. The following example will serve to make the method clear.

**Example.** A certain weight of oxygen *collected over water* measured 300 cc. under a pressure of 740 mm. and a temperature of 25° (298° A.). What would be the volume of the pure oxygen under standard conditions (0°, 760 mm.)? The vapor pressure at 25° is 23.69 mm. (see Appendix). Subtracting this from 740 gives 740 - 23.69, or 716.31, which is the pressure in millimeters under which the pure oxygen would occupy a volume of 300 cc. Now substitute the values in the equation (p. 59)

$$\frac{VP}{T} = \frac{V'P'}{T'}$$

$$\frac{300 \times 716.31}{298} = \frac{V' \times 760}{273}$$

$$V' = 258.9 \text{ cc.}$$

**The meaning of laws in science.** The law of Boyle and the law of Gay-Lussac are merely general statements in regard to the conduct of gases *as determined by experiment*. Like all other natural laws, they offer no explanation of the facts which they state, nor do they place any restriction upon nature which compels obedience, as the laws enacted by a legislature bind society. They are simply concise statements of what might be called the habits of nature as observed in experiment.

**Forming a theory.** Now that we have found it possible to state in concise form (laws) the conduct of gases under varying conditions of temperature and pressure, many questions arise in our minds. Why do all gases expand and contract in the same way, regardless of their other widely differing properties? Why does heating a gas cause it to expand? How does a gas exert pressure? What makes a liquid evaporate?

To answer these questions we begin by a process of *imagination*. We imagine that the similar conduct of all gases is probably due to some simple mechanical structure which all gases share, and we try to form a mental picture of this structure which gives such strikingly simple laws. *The process of constructing a mental picture of this kind is called forming a theory.* Having constructed a mental picture that gives us a reasonably plausible idea of how a gas may be made up, and which, if true, would answer all our questions, we next set about securing experimental evidence tending to show that our theory really corresponds with the facts. If we can finally secure so much evidence that we can no longer doubt that our imagined picture (or theory) represents things as they really are, then our theory becomes a *truth* and an addition to the great body of our knowledge about nature. If we can get little evidence in support of our theory, we lose interest in it and consider it of small value.

**The kinetic theory of gases.** The theory that was developed about the middle of the last century to account for the properties of gases (and the evaporation of liquids) is known as the *kinetic theory*. So much evidence has been collected in support of this theory that no one any longer doubts that it is a truthful picture of things as they really are. The chief points in this theory may be stated thus:

1. All gases are made up not of continuous matter but of extremely minute particles relatively far apart in proportion to their diameters. These particles are called *molecules*. The American scientist Millikan has calculated that 1 cc. of a gas under standard conditions contains in round numbers 27 billion billion molecules. This assumption satisfactorily accounts for the fact that gases may be compressed, since pressure merely crowds the molecules closer together.

2. The molecules are in constant motion in straight lines and with very high *average* velocities, and they have many collisions with each other and with the sides of the containing

vessel, rebounding without loss of velocity. For example, the molecules of hydrogen have an *average* velocity of about a mile per second at ordinary temperatures. This assumption makes it clear how a gas exerts a pressure upon the sides of the containing vessel (the impact of the molecules); why the effect of diminishing the volume is to increase the pressure (Boyle's law), for in the smaller volume more molecules will strike the sides of the vessel; and why gases tend to expand when there is no obstacle in the path of the molecules.

3. When we heat a gas we merely increase the average velocity of the molecules. If the volume is kept the same, more molecules will strike the sides of the vessel per second, and the pressure will be increased. To keep the pressure constant, the volume must be increased (law of Gay-Lussac).

4. In a later chapter we shall be able to prove that all the molecules of a given kind of gas have the same weight, but that those of different gases have different weights. We can also prove that the molecules of smallest weight move the fastest, while heavier molecules move more slowly, and that the velocity and the mass of each molecule are so related that all kinds of molecules have the same *average* kinetic energy.

5. The molecules of a liquid are also in motion, but they are close together and have a great attraction for one another. Nevertheless, from the surface of a liquid fast-moving molecules make their escape, and this constitutes *evaporation*. Since only fast-moving molecules can escape, the process of evaporation is necessarily a slow one under ordinary conditions.

**Avogadro's principle.** If all kinds of molecules possess the same *average* kinetic energy, they must all exert the same pressure upon the sides of the vessel, regardless of their kind (Boyle's law), and it must follow that *equal volumes of all kinds of gases contain the same number of molecules*. This last assumption was suggested by the Italian physicist Avogadro (Fig. 31) and is known as *Avogadro's principle*. It was first

offered merely as a plausible guess in explanation of the conduct of gases, but we now have conclusive proof of its truth. It has been of the greatest importance in the development of chemical theory.



FIG. 31. Amedeo Avogadro  
(1776-1856)

Professor in the University of Turin, Italy. Renowned for formulating the fundamental principle of modern chemistry known as Avogadro's principle. From a photograph of a statue erected to his memory in Turin

**Value of a theory.** When a theory is advanced, it is a first attempt to imagine an explanation for things that we do not understand. If we stop here, we have merely a guess or a speculation, and the theory has no value. A successful theory at once suggests many experiments and is a center about which much knowledge gradually accumulates. The definite picture presented by the theory assists us in holding all these facts together in relation to each other. We have a definite object in view in all our experiments, and as a rule we can either prove that the theory corresponds to the real truth or that it is so faulty as to require a new start with a new theory. Forming theories is therefore one of the most important means of gaining scientific knowledge, provided we make the proper use of the theory.

### EXERCISES

1. Why does a balloon tend to fall at night and rise at midday?
2. Why is the bottom of a balloon left open and not tightly closed?
3. How can you change the readings on the Fahrenheit scale into readings on the centigrade scale?
4. What evidence can you give tending to show that the amount of water vapor taken up by the atmosphere increases with the temperature?
5. Why does the carburetor on a motor car have to be adjusted with changes in atmospheric conditions, to secure the greatest efficiency?



6. From your experiences, state whether the compression of gases, as well as their expansion, is attended by any change of temperature. Explain fully.

7. A gas measures 200 cc. when subjected to a pressure of 740 mm. What volume will it occupy if the pressure is increased to 760 mm., the temperature remaining constant?

8. A gas measured 150 cc. in a laboratory in which the temperature was  $18^{\circ}$ . What volume will the gas occupy if the temperature is reduced to  $0^{\circ}$ , the pressure remaining constant?

9. A certain volume of gas is measured when the temperature is  $20^{\circ}$  and the pressure 740 mm. (a) At what temperature would its volume be doubled, the pressure remaining constant? (b) At what pressure would its volume be doubled, the temperature remaining constant?

10. A certain weight of hydrogen, subjected to atmospheric pressure, occupied a volume of 1250 cc. in a laboratory in which the readings of the thermometer and barometer were  $18^{\circ}$  and 746 mm. respectively. (a) What volume would this gas occupy under standard conditions? (b) Calculate the weight of this volume of hydrogen.

11. A gas subjected to atmospheric pressure occupied a volume of 1000 cc. in a laboratory at  $20^{\circ}$  and 740 mm. The next day the temperature of the laboratory fell to  $12^{\circ}$ , while the barometric pressure increased to 752 mm. What volume did the gas occupy under these conditions?

12. (a) 2500 cc. of oxygen measured over water at  $20^{\circ}$  and 740 mm. would occupy what volume under standard conditions? (b) Calculate the weight of this volume of the gas. (c) What weight of potassium chlorate would be required to prepare this amount of oxygen?

13. I wish to prepare 100 liters of hydrogen, measured over water in a laboratory where the temperature and pressure are respectively  $15^{\circ}$  and 750 mm. What weight of hydrogen sulfate will be required?

14. Oxygen was compressed in a 50-liter cylinder at  $20^{\circ}$  until the pressure was equal to 100 atmospheres. What volume would this occupy under a pressure of 1 atmosphere, the temperature remaining constant?

15. Suppose that the cylinder of oxygen referred to in problem 14 were heated to  $500^{\circ}$  during a fire. What pressure would the gas exert at this temperature?

16. An automobile tire having a capacity of 1200 cu. in. is inflated to a pressure of 70 lb. per square inch. The temperature of the air at the time of inflation is  $15^{\circ}$ , but on rapid driving the temperature is increased to  $40^{\circ}$ . What is the pressure now exerted by the air in the tube, assuming that the volume of the tire remains constant?



## CHAPTER VI

### WATER ; HYDROGEN PEROXIDE

**Introduction.** Of all the compounds with which we are acquainted, water is perhaps the best known. Because it is essential to all forms of life, both animal and vegetable, and to our welfare in many ways, it is important for us to study in detail the facts concerning this compound. In the form in which it occurs in nature it is never entirely pure, although it is not difficult to free it from its impurities.

**Properties of water.** Pure water is an odorless and tasteless liquid, colorless in thin layers but having a bluish tinge when observed through a considerable thickness. It solidifies at  $0^{\circ}$  and boils at  $100^{\circ}$  under the normal pressure of 1 atmosphere (barometric pressure of 760 mm.). If the pressure on the water is diminished, the boiling point is correspondingly lowered. Thus, on top of Mount Everest (29,000 ft. high) the barometric pressure is only 255 mm., and at this pressure water boils at  $72^{\circ}$ . When water is cooled, it steadily contracts, gradually increasing in density until the temperature of  $4^{\circ}$  is reached ; at lower temperatures it expands and so decreases in density. Water is remarkable for its ability to dissolve other substances and is the most general solvent known. Even such substances as glass and various kinds of rocks which are ordinarily regarded as insoluble dissolve in water, but to a very limited extent. Chemists usually employ aqueous solutions of substances rather than the substances themselves, since, as a rule, chemical action takes place more readily in solution.

**Occurrence.** The great abundance and wide distribution of water are facts familiar to all. Vast areas of the colder regions

of the globe are covered with it in the form of ice, while in the liquid state it covers about five sevenths of the earth's surface, reaching in some places a depth of nearly six miles. Large quantities occur in the soil, and as a vapor it is an essential constituent of the atmosphere. It likewise constitutes more than half the weight of living organisms. For example, nearly 70 per cent of the human body is water. All our foods contain more or less water. Thus, on an average, potatoes contain 78 per cent, apples 84 per cent, and tomatoes as high as 94 per cent of water.

**Historical.** Following the discovery of hydrogen, Cavendish made a careful study of the properties of the gas. In the course of his experiments he exploded a mixture of hydrogen and oxygen and observed that a small amount of a dewlike substance was formed. He was able to obtain a sufficient quantity of the liquid to make a study of its properties, and showed that it was pure water. Cavendish did not perceive the full meaning of his discovery, however, and it remained for Lavoisier, a few years later, to repeat and properly interpret the experiments of Cavendish. He proved beyond doubt that the water which Cavendish had obtained resulted from the union of the hydrogen and oxygen, and therefore that *water must be regarded as a compound of these two elements.*

**Composition of natural waters.** Water as it occurs in nature always contains more or less matter derived from the rocks and soils with which it comes in contact. When such water is evaporated, this matter is left behind in solid form. Even rain water, which is the purest natural water, contains dust particles and gases dissolved from the atmosphere. The foreign matter in natural waters is of two kinds: namely, *mineral* and *organic*.

1. **Mineral matter.** The amount and nature of the mineral substances present in any given water vary with the nature of the rocks and soil with which the water has been in contact. The mineral substances ordinarily present in fresh waters are common salt and compounds of calcium, magnesium, and iron.

Water containing any considerable quantities of mineral matter does not form a lather with soap; it is called *hard water* or, if a large amount of mineral matter is present, *mineral water*. Water containing little or no mineral matter, such as rain water, is termed *soft water*. One liter of an average river water contains about 0.175 g. of mineral matter. The water of the ocean contains about 40 g. of mineral matter to the liter, more than three fourths of which is common salt. The water of Great Salt Lake contains from 150 to 200 g. of mineral matter in 1 liter.

2. **Organic matter.** In addition to mineral matter natural waters contain more or less organic matter in solution or held in suspension. This consists not only of inanimate matter, derived from the decay of organic bodies on the earth's surface or present in sewage, but also of certain forms of living micro-organisms which usually accompany such products. Waters taken from shallow wells or streams in thickly populated districts are likely to contain a considerable quantity of such matter.

**Effect of the foreign matter in water upon health.** As a rule any sickness resulting from drinking impure waters is due to the presence of living microorganisms. Many of these are without injurious effect upon the human system, but some are the direct cause of disease. Thus, a transmissible disease such as typhoid fever is due to a certain kind of organism which, through food or drink, is introduced into the system. *It is easily possible for these organisms to find their way, through sewage, from persons afflicted with the disease into wells or any poorly protected water supply, and it is chiefly in this way that typhoid fever is spread.* It may be added that the appearance of a water gives no conclusive evidence as to its purity. A water may be unfit for drinking and yet be clear and odorless. No reliance can be placed on the simple methods sometimes described for testing the purity of water. Only the trained chemist and bacteriologist can carry out such methods for testing water as are trustworthy.

**Purification of water.** For purifying water on a small scale the processes of *distillation*, *boiling*, and *filtration* are commonly used. Other processes are used when it comes to purifying water on a large scale, as in the case of city water supplies. These processes will be discussed in a later chapter (Chapter XXXVII).

1. **Distillation.** The most effective way of purifying ordinary water is by the process of distillation. This consists in boiling the water and condensing the resulting steam. In the laboratory the process is usually conducted as follows:

**Laboratory distillation.**

Ordinary water is poured into the flask *A* (Fig. 32) and boiled. The steam is conducted through the *condenser* *B*, commonly known

as a Liebig condenser, which consists essentially of a narrow glass tube sealed within a larger one, the space between the two being filled with cold water, which enters at *C* and escapes at *D*. In this way the inner tube is kept cool and the steam in passing through it is condensed. The water formed by the condensation of the steam collects in the receiver *E*.

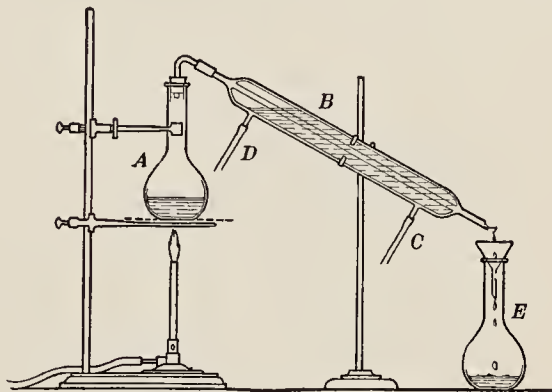


FIG. 32. The distillation of water as carried on in the laboratory

The water formed by the condensation of steam is known as *distilled water*. The mineral matter present in the original water is not *volatile* (capable of being changed into vapor) and remains in the container in which the water is boiled. The organic matter is also largely left in the container. A small amount of it, however, may be decomposed into volatile products, and these will pass over with the steam and be present in the distilled water. The percentage of such matter in distilled water is so small, however, that it is without effect

in most of the chemical processes in which pure water is employed; in a very few cases, in which extreme purity is required, further treatment is necessary.

Distilled water is used by the chemist in almost all the work of the chemical laboratory. Large quantities are also used in the manufacture of ice, as well as for drinking.

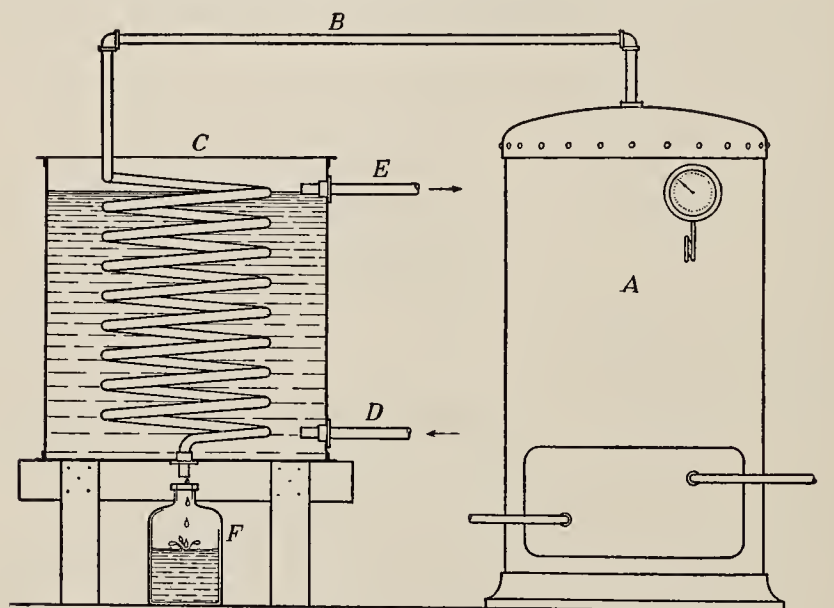


FIG. 33. The distillation of water for commercial purposes

**Commercial distillation.** In preparing distilled water on a large scale the steam is generated in a metal boiler *A* (Fig. 33) and is conducted through the pipe *B* to the condensing coil *C*, made of tin. This pipe is wound into a spiral and is surrounded by cold water, which enters at *D* and flows out at *E*. The distilled water is collected in a suitable container *F*.

**2. Boiling.** In purifying water for drinking purposes it is only necessary to remove or destroy the microorganisms present. When the amount of water to be purified is small, as is the case with the household supply for drinking, this is most conveniently accomplished by boiling the water for ten or fifteen minutes. While heat destroys the organisms in a short



time, severe cold even as low as  $100^{\circ}$  below zero has been found to have comparatively little effect upon them.

3. **Filtration.** On a small scale, water is filtered in two ways: (1) by passing it through some porous material, such as charcoal, or (2) by forcing it through porous clay ware, as is done in the Chamberlain-Pasteur filter. While such filters, if kept clean and in good condition, remove most of the organic matter, they do not remove mineral matter except such as is held in suspension. These household filters are not easily kept in order and soon become ineffective. They are no longer used to any great extent.

**Chemical conduct.** Water is a very stable substance; in other words, it does not undergo decomposition readily. To decompose it into its elements by heat alone requires a very high temperature. Even at  $2500^{\circ}$  only about 10 per cent of the water heated is decomposed, and, on cooling, the constituent gases again combine to form water. Though very stable toward heat, water can be decomposed in other ways, as by the action of the electric current or by certain metals.

Though containing 88.81 per cent of oxygen, water is not a good oxidizing agent, because of its great stability. Certain metals, however, as well as carbon, can be oxidized by very hot steam, the hydrogen being set free in gaseous form.

Water combines directly with many compounds, forming compounds called *hydrates*. Blue vitriol and alum are good examples of such hydrates. A substance that contains no water whatever is said to be *anhydrous*. The term *anhydrous* literally signifies *without water*.

**Heat of formation and heat of decomposition are equal.** The fact that a very high temperature is necessary to decompose water is in accord with the fact that great heat is evolved in its formation (p. 50), for it has been proved that the heat necessary to decompose, say, 1 gram of a compound into its elements (*heat of decomposition*) is equal to the heat evolved in the formation of 1 gram of the same compound from its elements (*heat of formation*).

**The determination of the exact composition of water.** Many very careful experiments have been made for the purpose of determining, with as great accuracy as possible, the ratio in which hydrogen and oxygen are present in water, and it is worth our while to study somewhat in detail the methods which have been employed, since they serve to illustrate in a general way the methods used in determining the composition of other compounds.

Two general methods of procedure are available for determining the composition of a compound: first, *the method of analysis*, in which a given weight of the compound is separated either directly or indirectly into its constituent elements and the identity and weight of each determined; second, *the method of synthesis*, which consists in determining the proportion in which the constituent elements unite to form the compound. Synthesis is therefore just the opposite of analysis.

1. **Methods based on analysis.** It will be recalled that water may be easily decomposed into its constituents by the electric current. It would seem probable that the exact composition of water could be determined easily in this way, since the volumes of the gases liberated can be measured with accuracy; and if we know their densities we can calculate their weights. When the experiment is carried out, however, the results obtained are not concordant, although in general the volume of the hydrogen liberated is slightly more than double the volume of the oxygen. Experiments prove that the method is subject to error from several sources. For example, the water through which the liberated gases bubble dissolves more of the oxygen than of the hydrogen. The ratio between the amounts of hydrogen and oxygen obtained in this process, therefore, does not represent with great accuracy the ratio in which they are combined in water. More accurate results are obtained by the methods of synthesis described in the succeeding paragraphs.

2. **Methods based on synthesis.** In the synthetic methods we determine the quantities of oxygen and hydrogen which

combine directly to form water. A description of the method as carried out for purposes of illustration in the lecture room will serve to show the general principle involved.

**Laboratory synthesis of water.** The combination of the two gases is brought about in a tube called a *eudiometer*. This is a graduated glass tube about 60 cm. long and 2 cm. wide, closed at one end (Fig. 34). Near the closed end two platinum wires are fused through the glass, the ends of the wires within the tube being separated by a space of 2 or 3 mm. The tube is entirely filled with mercury and inverted in a vessel of the same liquid. Pure hydrogen is passed into the tube until it is about one fourth filled. The tube is then lowered until the mercury stands at the same level inside and outside the tube, and the reading of the volume of the hydrogen is taken. Approximately an equal volume of pure oxygen is then introduced, and the volume is again noted. This gives the total volume of the two gases. From this the volume of the oxygen introduced may be determined by subtracting from it the volume of the hydrogen.

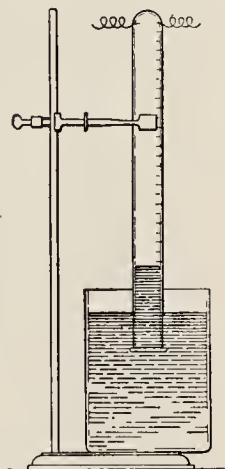


FIG. 34. A simple form of eudiometer

The combination of the two gases is now brought about by connecting the two platinum wires with an induction coil and passing a spark from one wire to the other. Immediately a slight explosion occurs. The mercury in the tube is at first depressed, because of the expansion of the gases due to the heat generated, but it at once rebounds, taking the place of the gases which have combined to form water. The volume of the water in the liquid state is so small that it may be disregarded in the calculations.

In order that the temperature of the residual gas and the mercury may become uniform, the apparatus is allowed to stand for a few minutes, and the volume of the gas is taken. The residual gas is then tested in order to ascertain whether it is hydrogen or oxygen, since experiments have proved that it is never a mixture of the two. From the information thus obtained the composition of the water may be calculated.

**Calculation of composition.** Thus, suppose the readings were as follows :

Volume of hydrogen . . . . .	20.3 cc.
Volume of hydrogen and oxygen . . . . .	38.7 cc.
Volume of oxygen . . . . .	18.4 cc.
Volume of gas left after combination has taken place (found to be oxygen) . . . . .	8.3 cc.

We have thus found that 20.3 cc. of hydrogen has combined with 18.4 cc. minus 8.3 cc. (or 10.1 cc.) of oxygen; or approximately 2 volumes of hydrogen has combined with 1 volume of oxygen. Since oxygen is 15.9 times as heavy as hydrogen, the proportion by weight in which the two gases combine is 1 part of hydrogen to 7.94 parts of oxygen.

**A more convenient form of eudiometer.** A form of eudiometer represented in Fig. 35, and different from that shown in Fig. 34, is sometimes used, since it is easier by means of this to obtain the gases under the same conditions of temperature and pressure in order to make comparisons. With this apparatus it is easily possible to take the readings of the volumes under the same conditions of temperature and pressure, and thus compare them directly. The apparatus is filled with mercury and the gases are introduced into the tube *A*. The experiment is carried out like the preceding one, except that, before taking the reading of the gas volumes, mercury is either added to the tube *B* or withdrawn from it by means of the stopcock

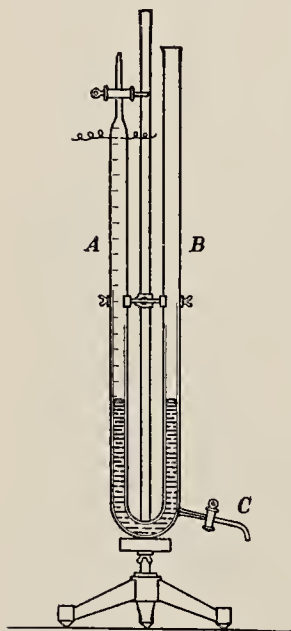


FIG. 35. A convenient form of eudiometer

*C*, until it stands at exactly the same height in both tubes. The gas inclosed in tube *A* is then under atmospheric pressure. The temperature of the gas, as well as the pressure to which it is subjected, being the same at the conclusion of the experiment as at the beginning, the volumes of the hydrogen and oxygen and of the residual gas may be directly compared as read off from the tube.



**Method used by Berzelius and Dumas.** The work of Berzelius and Dumas is of interest from a historical standpoint, since they were the first to determine the composition of water with any great accuracy. The method used is a very ingenious one, the weights of the hydrogen and oxygen being determined by indirect methods and not by direct weighing of the gases, which is not easily done. The method was first used by Berzelius in 1820, and later, in 1843, with greater refinement, by Dumas.

**Details of the experiment.** Fig. 36 illustrates the essential parts of the apparatus used in making the determination. The glass tube *B* contains copper oxide, while the tubes *C* and *D* are filled

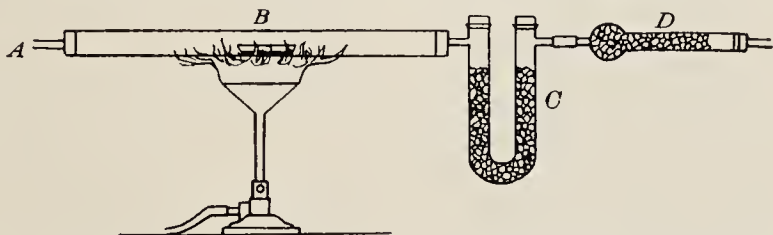


FIG. 36. Apparatus for determining the ratio by weight in which oxygen and hydrogen combine to form water

with calcium chloride, a substance which has great affinity for water. The tubes *B* and *C*, including their contents, are carefully weighed, and the apparatus is connected as shown in the figure. A slow current of pure *dry* hydrogen is then passed through *A*, and that part of the tube *B* which contains copper oxide is carefully heated. The hydrogen combines with the oxygen of the copper oxide to form water, which is absorbed by the calcium chloride in tube *C*. The calcium chloride in tube *D* prevents any moisture from entering tube *C* from the air. The operation is continued until an appreciable amount of water has been formed. The tubes *B* and *C* are then weighed once more. The loss of weight in the tube *B* will exactly equal the weight of oxygen taken up from the copper oxide in the formation of the water. The gain in weight in the tube *C* will exactly equal the weight of the water formed. The difference in these weights will of course equal the weight of the hydrogen present in the water formed during the experiment.



**Dumas's results.** The results secured by Dumas in 1843 may be summed up as follows:

Weight of water formed . . . . .	945.439 g.
Weight of oxygen given up by the copper oxide . . . .	840.161 g.
Weight of hydrogen present in the water . . . . .	105.278 g.

According to this experiment the ratio of hydrogen to oxygen in water is 105.278:840.161, or 1:7.98.

**Morley's results.** In more recent years the American chemist Morley (Fig. 37) has determined the composition of water with



FIG. 37. Edward Williams Morley  
(1838-1923)

Late professor of chemistry in Western Reserve University. Known for his accurate determinations of the densities of oxygen and hydrogen and of the ratio in which they combine to form water

great care. Extreme precautions were taken, and the hydrogen and oxygen which combined, as well as the water formed, were all accurately weighed. According to Morley's results 1 part by weight of hydrogen combines with 7.94 parts by weight of oxygen to form water.

#### Comparison of results obtained.

From what has been described it is easy to see that it is by experiment alone that the composition of a compound can be determined. Different methods may lead to slightly different results. The more accurate the method chosen, and the greater the skill with which the experiment is carried out, the more accurate will be the results. It is generally conceded by chemists that

the results obtained by Morley are the most accurate. In accordance with these results, then, *water must be regarded as a compound containing hydrogen and oxygen in the ratio of 1 part by weight of hydrogen to 7.94 parts by weight of oxygen.*

Relation between any given volume of water vapor and the volumes of the hydrogen and oxygen which combine to form it. When the quantitative synthesis of water is carried out at ordinary temperatures, the water vapor formed by the union of the hydrogen and oxygen at once condenses. The volume of the resulting liquid is so small that it may be disregarded

in making the calculations. If, however, the experiment is carried out at a temperature of  $100^{\circ}$  or above, the water vapor formed is not condensed, and it then becomes possible to compare the volume of the vapor with the volumes of hydrogen and oxygen

which combined to form it. In this way it has been proved that 2 volumes of hydrogen and 1 volume of oxygen combine to form 2 volumes of water vapor, the volumes all being measured under the same conditions of temperature and pressure. It will be noted that the relation between these volumes may be expressed by whole numbers. It will be found from subsequent discussions that a similar statement holds in reference to all gaseous elements which combine with each other.

**Laboratory details.** The form of apparatus used in determining the relation between the volumes of hydrogen and oxygen uniting and that of the aqueous vapor formed is illustrated in Fig. 38. The arm *A* of the eudiometer in which the combination of the gases is effected is surrounded by a tube through which is passed

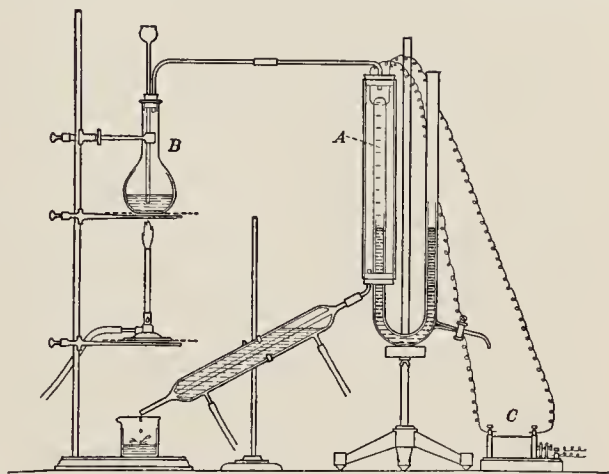


FIG. 38. Apparatus for determining the ratio by volume in which oxygen and hydrogen combine, and the ratio of each of these volumes to the volume of the steam formed

steam or, preferably, the vapor of some liquid boiling above  $100^{\circ}$  (amyl alcohol is often used). A mixture of 2 volumes of hydrogen with 1 volume of oxygen is introduced into the eudiometer. A suitable liquid is then boiled in the flask *B*. The resulting vapor is conducted through the space between the tube *A* and the outer tube, and is then condensed as shown in the figure. When the volume of the mixed gases in *A* has become stationary, showing that the temperature of the gases is the same as that of the vapor, and the pressure adjusted as in the former experiment (see Fig. 35 and description), the reading on the eudiometer tube is noted. The union of the two gases is then effected by an electric spark from an induction coil *C*. After the union has taken place, the pressure is adjusted and the reading again noted after the volume of the vapor has become constant. The volume of the vapor thus obtained can be compared directly with the volumes of the hydrogen and oxygen which united to form it.

**The law of definite composition.** Attention has been called to the fact that chemical processes involve definite weights of matter (p. 38). We have now seen that chemically pure water has a perfectly definite composition. It makes no difference what the source of the water is. Whether it is obtained from the melting of pure ice, from the condensation of steam, or from the direct combination of hydrogen and oxygen, its composition is always exactly the same; namely, 1 part by weight of hydrogen and 7.94 parts by weight of oxygen, or, expressed in percentages, 11.19 per cent of hydrogen and 88.81 per cent of oxygen. A similar statement has been found to hold good for every pure compound. Thus, experiments have shown that potassium chlorate always contains 31.90 per cent of potassium, 28.94 per cent of chlorine, and 39.16 per cent of oxygen, while mercuric oxide contains 92.61 per cent of mercury and 7.39 per cent of oxygen. This truth regarding the constancy of composition of chemical compounds is known as the *law of definite composition* and may be expressed as follows: *The composition of a pure compound is always precisely the same.*

**History of law of definite composition.** The common experiences of the earlier chemists led them to believe that the composition of a pure compound is quite definite. The question as to whether this is so or not became an important issue in the years 1802-1808, as a result of the views of a distinguished Frenchman, Berthollet. On theoretical grounds Berthollet was led to believe that the composition of a substance is somewhat variable, being dependent on the relative quantities of the several materials present at the time of its formation.

These views were strongly opposed by a fellow countryman, Proust, who was professor of chemistry at Madrid during most of the controversy. Proust maintained that the composition of a pure compound is perfectly definite, and that when two elements form more than one compound, each has its own exact composition, there being no intermediate gradations. He maintained that apparent variability is due to lack of purity in the compound or to the unavoidable errors in the methods of analysis. Proust's experimental work was very accurate for his time, but his analyses were subject to errors of from 1 to 2 per cent. The advance in experimental exactness has steadily demonstrated the correctness of Proust's conclusions. In 1860 and again in 1866 the Belgian chemist Stas undertook elaborate researches in a critical study of the law of definite composition, his analyses being trustworthy in some instances to within about 1 part in 50,000. Within these limits he showed that the law holds rigidly. In our own time the work of the American chemist Theodore Richards has demonstrated the accuracy of the law within still narrower limits.

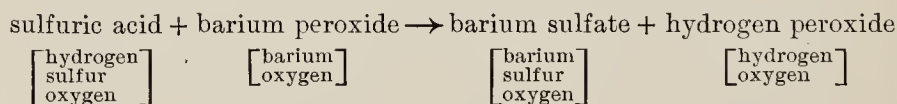
**Hydrogen peroxide.** In 1818, while studying the action of acids upon certain oxides, the French chemist Thénard discovered the compound which we now call hydrogen peroxide. The pure compound is a liquid and, like water, is composed of hydrogen and oxygen. The proportions in which the hydrogen and oxygen are present in these two compounds, however, are widely different, as shown in the following statement:

Water . . . . .	1 part of hydrogen to 7.94 parts of oxygen, by weight
Hydrogen peroxide . . . . .	1 part of hydrogen to 15.88 parts of oxygen, by weight



In other words, the weight of oxygen *combined with a fixed weight of hydrogen* is just twice as great in hydrogen peroxide as in water. This larger percentage of oxygen is indicated by the name *peroxide*, the prefix *per-* meaning "more" or "excess."

**Preparation of hydrogen peroxide.** While a dilute solution of hydrogen peroxide may be easily obtained, the pure compound cannot be prepared without great difficulty, since it decomposes into water and oxygen with explosive violence. Dilute solutions of the compound are prepared by the action of sulfuric acid on barium peroxide. The reaction may be represented as follows:



It will be noted that in this reaction the barium of the barium peroxide changes places with the hydrogen of the acid. The barium sulfate formed is insoluble, while the hydrogen peroxide dissolves in the water present. The barium sulfate may therefore be removed from the solution by filtration. In this way one can readily prepare a dilute solution of the peroxide in water. In this form it is a common article of commerce.

**Properties of hydrogen peroxide.** Hydrogen peroxide is a clear, sirupy liquid having a density of 1.44 at 20°C. Because of the highly explosive character of the pure compound it is prepared in the form of a dilute solution in water.

Since hydrogen peroxide so readily decomposes, with evolution of oxygen, it acts as a strong oxidizing agent even in very dilute solutions. An easily oxidizable substance like wool is ignited by the addition of a few drops of the pure compound. The speed of decomposition of hydrogen peroxide is influenced in many ways. In dilute solutions and at a low temperature the speed is very slow, while at higher temperatures and in more concentrated solutions it becomes so great as to cause violent explosions. Moreover, the speed of decomposition is greatly affected by the presence of certain catalytic



agents (p. 29). Thus, a little finely divided platinum or manganese dioxide, added to a concentrated solution of the peroxide, produces such rapid decomposition as to cause an explosion. Certain organic substances have a similar action. Just as some substances increase the rapidity of decomposition, so others retard it. Thus, the ordinary solution of hydrogen peroxide sold for medicinal purposes contains a small amount of some such substance, generally a trace of acid, which is added to preserve the strength of the solution by retarding decomposition. Catalytic agents that retard the speed of a reaction are known as *negative* catalyzers to distinguish them from *positive* catalyzers, which increase the speed of a reaction.

**Uses.** Hydrogen peroxide has many commercial uses, all based on its strong oxidizing properties. The common medicinal peroxide of the druggist is an aqueous solution containing 3 per cent, by weight, of the peroxide and 97 per cent of water. It has long been used as an antiseptic, but recent experiments indicate that its efficiency for this purpose has been greatly overrated. It acts upon certain dyes and natural colors, such as that of the hair, oxidizing them into colorless compounds; hence it is sometimes used as a bleaching agent. The chemist finds it especially useful as an oxidizing agent in many analytical operations. For this purpose it is often convenient to have a rather concentrated solution, so that a 30 per cent solution is now sold as a commercial product.

**The law of multiple proportion.** We have seen that both water and hydrogen peroxide are compounds of hydrogen and oxygen, and that the ratio by weight in which these two elements are present in each of these compounds is as follows:

Water . . . . .	hydrogen : oxygen = 1 : 7.94
Hydrogen peroxide . . . . .	hydrogen : oxygen = 1 : 15.88

It will be seen that the ratio between the weights of oxygen combined with a fixed weight of hydrogen (say 1 g.) in these two compounds is 7.94 : 15.88, or 1 : 2.

Similarly, many elements other than oxygen and hydrogen unite to form a number of distinct compounds, each with its own precise composition. In all such compounds the same statement holds as in the case of water and hydrogen peroxide; the weights of the one element which are combined with a *fixed weight* of the other always bear a simple ratio to each other, such as 1 : 2 or 2 : 3. This truth is known as *the law of multiple proportion*. It was formulated by John Dalton (p. 61) in 1808 and may be stated thus: *When any two elements, A and B, combine to form more than one compound, the weights of A which unite with any fixed weight of B bear the ratio of small whole numbers to each other.*

#### EXERCISES

1. Why does the chemist use distilled water, rather than filtered water, in making solutions?

2. How could you determine the total amount of solid matter dissolved in a sample of water?

3. How could you determine whether a given sample of water is distilled water?

4. How could the presence of air dissolved in water be detected?

5. How could the amount of water in a food such as bread or potato be determined?

6. Would ice frozen from impure water necessarily be free from disease germs?

7. Suppose that the maximum density of water were at  $0^{\circ}$  instead of  $4^{\circ}$ ; what effect would this have on the formation of ice on bodies of water?

8. In the experiment illustrated by Fig. 32, why is cold water passed into *C* instead of into *D*?

9. Mention at least two advantages that a metal condenser has over a glass condenser.

10. Draw a diagram of the apparatus used in your laboratory for supplying distilled water.

11. Distinguish between the terms *pure* and *chemically pure* as applied to any given sample of water.

12. From the following data determine the ratio in which oxygen and hydrogen unite, the volumes all being measured under the same conditions of temperature and pressure:

Volume of hydrogen in eudiometer . . . . .	19.34 cc.
Volume of oxygen and hydrogen . . . . .	48.23 cc.
Volume of gas (oxygen) left after explosion . . . .	19.22 cc.

13. Morley found the composition of water by determining the weights of hydrogen and oxygen that combine with each other to form water. The results of four trials are as follows:

HYDROGEN USED	OXYGEN USED	HYDROGEN USED	OXYGEN USED
(1) 3.2645 g.	25.9176 g.	(3) 3.8193 g.	30.3210 g.
(2) 3.2559 g.	25.8531 g.	(4) 3.8450 g.	30.5294 g.

In each case calculate the ratio in which the hydrogen and oxygen combined to form water.

14. The results of some of the individual experiments performed by Dumas in the determination of the composition of water are as follows (p. 77):

OXYGEN USED	WATER OBTAINED	OXYGEN USED	WATER OBTAINED
(1) 13.179 g.	14.827 g.	(3) 60.031 g.	67.586 g.
(2) 76.364 g.	85.960 g.	(4) 20.362 g.	22.905 g.

Calculate the composition of water as determined in each of the trials.

15. 20 cc. of hydrogen and 7 cc. of oxygen, measured in a eudiometer (Fig. 38) at  $110^{\circ}$ , are exploded. (a) How many cubic centimeters of water vapor are formed? (b) What gas and how much of it remains in excess?

16. (a) What weight of water is formed by the combustion of 100 liters of hydrogen, measured under standard conditions? (b) What volume of oxygen will be required in (a)? (c) What weight of potassium chlorate is necessary to prepare this amount of oxygen?

17. What weight of oxygen is present in 1 kg. of the ordinary hydrogen peroxide solution? In the decomposition of this weight of the peroxide into water and oxygen, what volume of oxygen (measured under standard conditions) is evolved?

## CHAPTER VII

### NITROGEN AND THE RARE ELEMENTS IN THE ATMOSPHERE

**Properties of nitrogen.** We have seen that oxygen is that constituent of the atmosphere which supports life. It is a very active element, however, and we can readily imagine what would happen if the atmosphere were all oxygen. This great activity of oxygen is kept in check by the presence in the atmosphere of a large percentage of the inert gas which we call *nitrogen*, which will neither burn nor support combustion. Like oxygen and hydrogen, nitrogen is a colorless, odorless, and tasteless gas. It is slightly lighter than oxygen, 1 liter of it weighing 1.2506 g. Its solubility in water is about the same as that of hydrogen, 1 liter of water dissolving about 23 cc. of the gas under standard conditions. At low temperatures and under great pressure nitrogen is obtained in the form of a colorless liquid. This liquid has a density of 0.8 and boils at  $-195.8^{\circ}$  under a pressure of one atmosphere. At a still lower temperature nitrogen may be obtained in the form of an icelike solid melting at  $-209.8^{\circ}$ .

**Occurrence.** Dry air is composed principally of oxygen and nitrogen in the free state, about 78 parts out of every 100 parts by volume being nitrogen. Nitrogen also occurs in nature combined with potassium and oxygen in the form of potassium nitrate (commonly called *saltpeter* or *niter*) ; it also occurs combined with sodium and oxygen in the form of sodium nitrate (Chile saltpeter). Nitrogen is likewise an essential constituent of all living organisms ; it is therefore a necessary constituent of our foods.

**Historical.** Nitrogen was discovered in 1772 by the Scottish chemist Rutherford, who obtained it from air by removing

the oxygen. A little later Scheele (Fig. 39) showed it to be a constituent of air, and Lavoisier gave it the name *azote*, signifying that it would not support life. The name *nitrogen* was afterward suggested because of its presence in saltpeter, or niter. The term *azote* and the symbol Az are still used by the French chemists.

**Preparation from air.** In the laboratory, nitrogen is prepared from air by the action of some substance that will combine with the oxygen, leaving the nitrogen free. It is necessary, however, to choose a substance that will combine with the oxygen to form a product which is not a gas and which can be readily separated from the nitrogen. The substances most often used for this purpose are phosphorus and copper.

1. *By the action of phosphorus.* The method used for the preparation of nitrogen by the use of phosphorus is as follows:

**Laboratory method.** The phosphorus is placed in a little porcelain dish (Fig. 40) supported on a cork and floated on water. It is then ignited by contact with a hot wire, and immediately a bell jar is brought over it so as to confine a portion of the air. The phosphorus combines with the oxygen to form an oxide of phosphorus known as phosphorus pentoxide. This is a white solid which floats about in the bell jar, but which in a short time is all absorbed by the water, leaving the nitrogen. The withdrawal of the oxygen is indicated by the rising of the water in the bell jar.



FIG. 39. Karl Wilhelm Scheele  
(1742-1786)

A Swedish chemist and one of the greatest of all times. He discovered oxygen independently of Priestley and showed it to be a constituent of air. He also discovered the elements chlorine, tungsten, and molybdenum and many important compounds



2. *By the action of copper.* The oxygen in the air may also be removed by passing air slowly through a heated tube containing copper. The copper combines with the oxygen to form copper oxide, which is a solid. The nitrogen passes on and may be collected over water (Fig. 41).

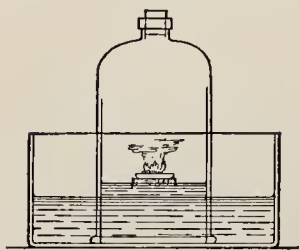


FIG. 40. Preparing nitrogen by burning out the oxygen of air with phosphorus

**Nitrogen from air impure.** The nitrogen obtained from air by the above methods is never quite pure, but contains about 1 per cent of a mixture of other gases (p. 90). The properties of the nitrogen, however, are not materially affected by the presence

of these gases. If we wish to obtain pure nitrogen we may do so by heating certain compounds of nitrogen.

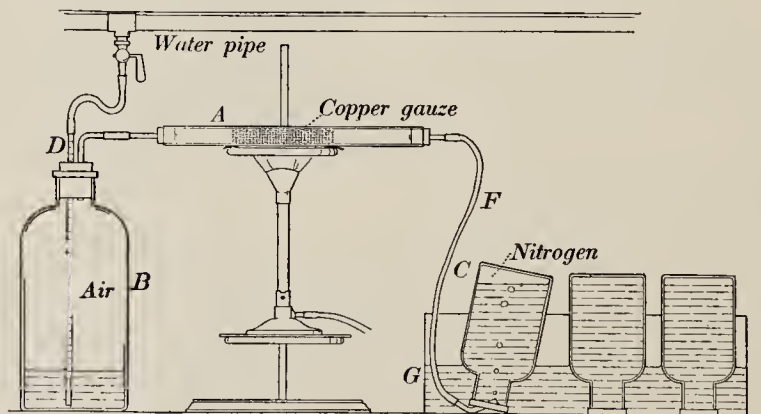


FIG. 41. Preparing nitrogen by removing the oxygen from air with hot copper

The copper is placed in the tube *A* and heated. Air is then forced slowly through the tube by letting water run into the bottle *B*. As the air passes through the tube the oxygen of the air combines with the hot copper, forming a black solid compound of copper and oxygen known as copper oxide, while the nitrogen passes on and is collected over water in the cylinder *C*

**Preparation from compounds.** The compound most commonly used for preparing nitrogen is composed of nitrogen, hydrogen, and oxygen, and is known as *ammonium nitrite*. When this

is heated the nitrogen is liberated in the free state, while the hydrogen and oxygen combine to form water.

ammonium nitrite  $\longrightarrow$  nitrogen + water

$\left[ \begin{array}{c} \text{nitrogen} \\ \text{hydrogen} \\ \text{oxygen} \end{array} \right]$

$\left[ \begin{array}{c} \text{hydrogen} \\ \text{oxygen} \end{array} \right]$

**Commercial methods of preparation.** It is evident that the method used for the preparation of oxygen from liquid air (p. 30) would serve equally well for the preparation of nitrogen. This method has come to the front through the development of more efficient machines for liquefying air. The large amount of nitrogen used in the manufacture of ammonia (see Haber Process) and of certain fertilizers is prepared by this method.

**Chemical conduct.** Nitrogen is much less active than oxygen, showing little or no tendency to combine with any other elements at ordinary temperatures. At higher temperatures it combines with magnesium, lithium, titanium, and a number of other elements. The compounds formed are in general called *nitrides*, just as compounds of an element with oxygen are called *oxides*. When nitrogen is mixed with oxygen and subjected to the action of electric sparks, the two gases slowly combine and form oxides of nitrogen. A mixture of nitrogen and hydrogen, when heated under proper conditions, forms ammonia, a gaseous compound of nitrogen and hydrogen. Since we are constantly inhaling nitrogen, it is evident that it is not poisonous. Nevertheless we should soon suffocate in an atmosphere of pure nitrogen, on account of the exclusion of the necessary oxygen.

**Uses of nitrogen.** The chief use of nitrogen is in the preparation of certain of its compounds. In the United States and Canada the compound most largely prepared from the free nitrogen is known as *calcium cyanamide*. This is valuable as a fertilizer and will be discussed in detail in a later chapter. In Germany a great deal of nitrogen is used in the preparation of ammonia, which in turn is used in the manufacture of

certain fertilizers and of nitric acid. In the United States we obtain our supplies of ammonia and nitric acid largely from other sources, but it is probable that at no very distant date we shall prepare at least a large proportion of our requirement of these compounds from nitrogen separated from the atmosphere.

**The assimilation of nitrogen by plants.** While nitrogen is an essential constituent of both plants and animals, yet, with the exception of a few plants, especially those belonging to the botanical order *Leguminosae*, these organisms have not the

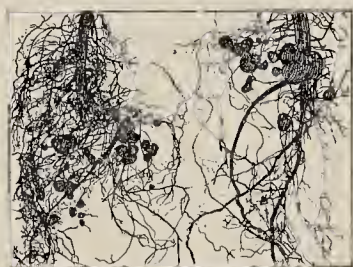


FIG. 42. Tubercles on the roots of bean plants

power of directly assimilating free nitrogen from the atmosphere, but obtain their supply from certain compounds of nitrogen. It has long been known that some of the leguminous plants, such as the beans, peas, and clover, not only thrive in poor soil but at the same time enrich it. Investigation has shown that these plants obtain at least a portion

of their supply of nitrogen from the atmosphere. The assimilation of nitrogen is accomplished through the agency of groups of microorganisms which produce little tubercles on the roots of the plants, as represented in Fig. 42. These microorganisms have the power of converting free nitrogen taken from the air into compounds of nitrogen, some of which are assimilated by the plant, while others are left in the soil and thus enrich it.

**Argon, helium, neon, krypton, xenon.** These are rare gaseous elements and occur in the air in very small quantities. They are similar in that they are all colorless, odorless gases. They differ from all other known elements in that they are entirely inactive, forming no compounds whatever. The following facts in regard to these elements are of interest:

1. **Argon.** This is the most abundant of the group. It was discovered in 1894 by two British scientists, Lord Rayleigh and Sir William Ramsay (Fig. 43). It is now prepared from liquid air and, like nitrogen, is used in certain gas-filled electric lamps.

2. **Helium.** In 1889 the American chemist Hillebrand found that certain minerals containing the element uranium evolve a gas when heated. He concluded, from a brief investigation, that the gas so evolved is nitrogen. In 1895, shortly after the discovery of argon, the attention of Ramsay was called to this experiment, with the suggestion that argon might be present in the gas which Hillebrand had obtained. Ramsay repeated the experiment, and upon examination it was found that the spectrum of the gas contained an orange-colored line identical with that which Janssen, in 1868, had detected in the spectrum of the gases surrounding the sun. Lockyer attributed this line to the presence of an unknown element in the sun's atmosphere, which he named *helium*, a word meaning "the sun." Ramsay's experiments proved that the gas evolved from the uranium minerals consists of this same element, helium, mixed with small percentages of argon and nitrogen. Ramsay then showed that traces of helium are present in the atmosphere. Later Cady found it in the natural gas issuing from certain wells in Kansas and Texas. It is the most difficult of all gases to liquefy and solidify. The boiling point of the liquid helium is  $-268.9^{\circ}$ . It was first solidified in 1926 by Keesom, professor in the University of Leiden, Holland.

3. **Neon, krypton, and xenon.** These three gases were discovered by Ramsay and Travers in 1898. They obtained them from liquid air, thus proving their presence in the atmosphere.

3. **The commercial manufacture of helium.** Until the year 1918 helium had been obtained in minute quantities only. When the

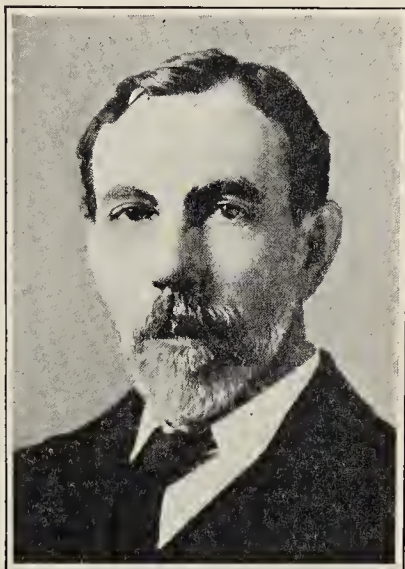


FIG. 43. Sir William Ramsay  
(1852-1916)

An English chemist, who, together with the English scientist Lord Rayleigh, discovered argon. In association with Travers he also discovered the elements xenon, neon, and krypton, and was the first to show that helium is a constituent of the atmosphere. For these and other outstanding discoveries Ramsay was given the Nobel prize in 1904



United States entered the World War an effort was made to find some noncombustible gas for filling observation balloons, since the records showed that 95 per cent of the casualties resulting from the use of such balloons was due to the highly combustible character of the hydrogen with which they were filled. Helium was the only gas that at all met the requirements, for it is noncombustible, and, although twice as heavy as hydrogen, its lifting power is

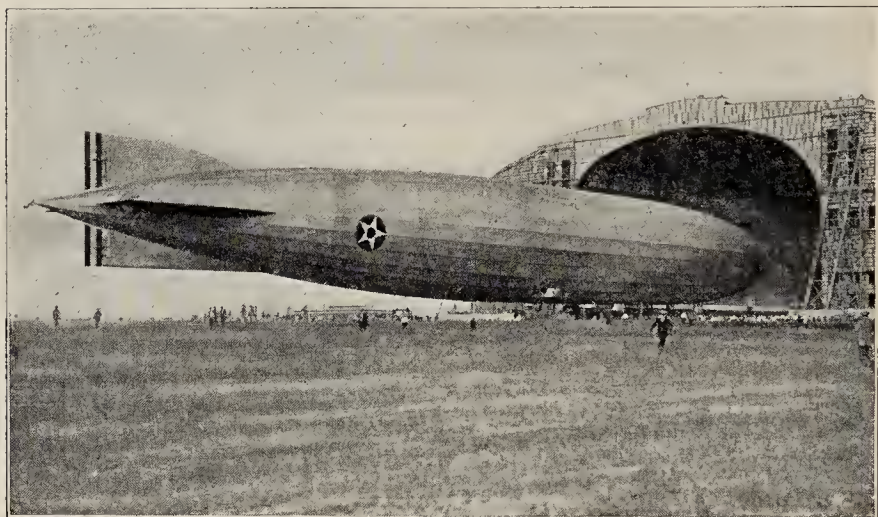


FIG. 44. The American dirigible *Shenandoah* leaving her hangar at Lakehurst, New Jersey

This airship (wrecked in a storm in 1925) was 207 meters long and was inflated with approximately 60,000 cubic meters of helium

about 93 per cent that of hydrogen. An effort was made, therefore, to obtain it from the natural gas found in certain localities in Texas, which contained about 1 per cent of helium. To separate the helium, advantage was taken of its very low boiling point. The problem was exceedingly difficult. When the armistice was signed, however, 250,000 cu. ft. of nearly pure helium, stored in steel cylinders, was on its way to our armies, and the gas, which at the beginning of the war was almost a chemical curiosity and cost about \$1700 per cubic foot, was being prepared in quantities at a cost of a few cents per cubic foot. At present a large government-owned plant located in Texas is separating from the natural gas of that locality sufficient helium to fill our dirigibles (Fig. 44).



TABLE OF RARE ATMOSPHERIC ELEMENTS

	HELIUM	NEON	ARGON	KRYPTON	XENON
Weight of 1 liter . . .	0.1785 g.	0.9002 g.	1.7824 g.	3.708 g.	5.851 g.
Boiling point of liquid form . . . . .	- 268.9°	- 245.9°	- 185.7°	- 151.8°	- 109.1°
Number of volumes in 1,000,000 volumes of air (approximate) . .	4.00	12.3	9400	0.5	0.06

## EXERCISES

1. How could you distinguish between oxygen, hydrogen, and nitrogen?

2. Calculate the relative weights of nitrogen and oxygen; of nitrogen and hydrogen.

3. In the preparation of nitrogen from the air, how would hydrogen do as a substance for the removal of the oxygen?

4. Why not prepare nitrogen by burning a candle in confined air?

5. What is the significance of each of the following names: argon, helium, neon, krypton, xenon? (Consult dictionary.)

6. Note some of the important discoveries made by Scheele (consult encyclopedia).

7. What weight of nitrogen can be obtained from 10 liters of air measured under the conditions of temperature and pressure which prevail in your laboratory?

8. A student prepared 25 liters of nitrogen collected over water in a laboratory in which the thermometer registered 20° and the barometer 742 mm. Calculate the volume of this nitrogen under standard conditions.

9. About 1000 cu. ft. of argon is being used daily in gas-filled lamps. What volume of air is required in its preparation, assuming that all the argon present can be secured?

## CHAPTER VIII

### MOLECULAR WEIGHTS; ATOMIC WEIGHTS

**Molecules.** We have seen that the way gases act, as described in the gas laws, proves beyond any doubt that every gas is made up of extremely small particles. These particles are called *molecules*. Methods have been devised for actually calculating the weights of the individual molecules with a good deal of accuracy, but these weights are so small that we can make little practical use of them. A few illustrations will help us, better than definite figures as to their actual weights, to realize how very small the molecules are.

Langmuir, an American scientist, has calculated that if the molecules in one cubic inch of air were each one to be changed into a grain of fine sea sand, the resulting sand would fill a trench a mile wide and three feet deep, reaching from New York to San Francisco. The English scientist Aston has shown that if we were to pierce an electric-light bulb with a minute hole, such that one million molecules of air could enter per second, it would take one hundred million years for enough air to enter to bring the pressure within the bulb to that of the outside atmosphere.

**Atoms.** A moment's reflection will make it clear that the molecules of a *compound*, such as water, must themselves be made up of parts, for a compound is composed of at least two different elements, and each molecule must have some of each constituent. *These constituent parts of a molecule are called atoms.* The molecules of any compound must consist of at least two atoms, and we shall see that most molecules have more than that. The atoms are therefore somewhat smaller

than the molecules. If we start with a cube of lead 10 cm. on an edge and first cut it into plates 1 atom thick, and then cut the plates into strips 1 atom wide, these strips placed end to end would reach 6,300,000,000,000 miles,—approximately the distance light will travel in a year.

The law of definite composition states the fact that the composition of any pure sample of a compound is always the same.

It must therefore be true that the molecules of the compound all contain the same number and kinds of atoms, for any weighable sample of the compound is merely a vast collection of molecules. It must also be true that the weights of the atoms of any one kind in all the molecules must be the same or, if slightly different, must *average* the same; otherwise the individual molecules would have different compositions and we should not have the law of definite composition. We shall see in Chapter XXI that the atoms of some elements all have the same weight, while those of other elements have somewhat different weights but are always mixed in a constant ratio, giving a constant *average* weight.



FIG. 45. John Dalton (1766-1844)  
English scientist and teacher, who  
developed the atomic theory

**The atomic theory.** From almost the earliest days of recorded history certain philosophers have argued that matter must be made up of individual particles called atoms, while others have argued against this view. As long as there was no way to decide the question, the argument was very useless. In the law of definite composition the English chemist John Dalton (Fig. 45) saw a real proof that matter must be made up of atoms, and in 1806 he revived the

atomic theory of matter based upon this law. We now have such convincing evidence that this picture of the make-up of matter is a true one that we accept it as a *truth* rather than as a theory, *for any theory becomes a truth when there is no longer any doubt as to its reality.*

**Relative molecular weights.** It will be recalled (p. 65) that the simplicity of the gas laws led Avogadro to believe that in any gas the molecules are so spaced apart that under given conditions of temperature and pressure equal volumes of any two gases inclose the same number of molecules, no matter what their individual weights may be. This is somewhat surprising, but so many facts supporting this view have come to our knowledge that there can be no doubt that Avogadro's principle is an approximate statement of the truth. We can determine the number of molecules in a given volume of any gas (say 1 cc.) with more precision than we can take the census of a large city, and we know that all gases have approximately the same number of molecules in 1 cc. under standard conditions of temperature and pressure. This number is  $2.7 \times 10^{19}$ , or 27 followed by eighteen zeros.

With the help of Avogadro's principle we can at once determine the *relative* weights of the molecules of various gaseous substances, and these relative weights are more useful to us than are the actual weights. We reason that in any definite volume of a gas (say 1 liter) there will always be the same number of molecules, no matter what gas fills the liter measure, provided the gases are measured under the same conditions of temperature and pressure. Consequently the weights of 1 liter of the different gases *will be in the same ratio* as those of the several kinds of molecules constituting the gases. Thus, a liter of oxygen weighs 1.429 g., a liter of hydrogen weighs 0.08987 g., and one of nitrogen weighs 1.2507 g. These figures give the actual weight in grams of *equal numbers* of the three kinds of molecules. They must therefore be *in the same ratio* as the actual weights of the three kinds of molecules.



**Relative atomic weights.** The next question is, Have we any simple way of determining *the relative weights of the atoms* that make up the molecules? At first sight it may appear that the law of definite composition gives us such a method. For example, we know that each sample of water we analyze consists of 1 part of hydrogen and 7.94 parts of oxygen *by weight*. Therefore the composition of *each molecule* must be expressed by this ratio. If it were true that water molecules are all made up of one atom each of hydrogen and of oxygen, then these two numbers, 1 and 7.94, would be the relative weights of the two kinds of atoms, and our problem would be solved. *These numbers that state the ratio in which two elements combine in a given compound are called the combining weights of the elements*, and they can be determined with great precision by the analysis of compounds, as we have seen in the case of water.

But there is another compound of hydrogen and oxygen, namely, hydrogen peroxide, and in this the ratio is 1 : 15.88 (p. 81), so that oxygen has *two* combining weights relative to hydrogen. Sometimes two elements will combine in five or six ratios and so have five or six combining weights. Here our trouble begins, for we have no direct way of deciding which of these compounds (if any) is the one which has one atom of each element in the molecule.

It will be noticed, however, that in the case of water and hydrogen peroxide *the one ratio is double that of the other*, giving oxygen the two combining weights, 7.94 and 15.88. Experiment shows that in all cases in which two elements combine to form two or more compounds a similar law holds true: the combining weights of any given element are all multiples of the smallest one. The atomic make-up of matter at once explains this striking fact. It is evident that in the molecules of a compound the atoms will always unite in some definite small ratio such as 1 : 1, 1 : 2, 2 : 3, etc. and all the combining weights will have to be multiples one of the other. It is clear that this is the explanation of the law of multiple proportion.

We have now made real progress in finding the relative weights of the atoms, for by experiments we can determine the combining weights of two elements, *and some one of these combining weights must be the real atomic weight.* Many years of effort to fix upon the right combining weight have shown that we must follow an unexpected plan. We must first get the *molecular weights of compounds* of the elements and from these draw conclusions as to which of the combining weights is the true *atomic weight* of the constituent atoms. Let us, therefore, now turn to the problem of getting the molecular weights of compounds.

**Standard for molecular weights.** When we have to deal with any series of purely relative values, such as molecular weights, we usually choose some one value as unity and express the others in terms of this one. For example, in our coinage we may select the dollar as our standard, and state the value of the other coins as fractions and multiples of this; or we may select the penny, and state the value of all others as multiples of this. We may select the dime and call it 10 or 25 or any number we choose, and calculate the value of all other coins to the standard we have selected. Whatever coin we select and whatever value we give it, *the ratio* in value between all the coins will remain unchanged.

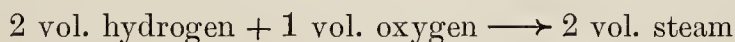
In a similar way we might call oxygen unity. The ratio by weight between the liter of oxygen (1.429 g.), hydrogen (0.08987 g.), and nitrogen (1.2506 g.) would then be 1 : 0.0629 : 0.875. But in general we should like to avoid numbers that are less than unity, just as we have avoided coining a halfpenny; so we might take the liter of smallest weight (hydrogen) as unity, and the ratios would then be 15.88 : 1 : 13.9. *Since oxygen plays such an important part in chemistry, we should like to stick to it as our standard,* while keeping the weights of all other molecules above unity. We can therefore adopt provisionally the round number 16 for oxygen, and the ratio then becomes 16 : 1.008 : 14.01.

By determining the weight of 1 liter of each of all known gases we can decide upon the relative weights of their molecules referred to this standard (oxygen = 16) or to any standard we may later adopt.

**Standard for atomic weights.** Since the molecules are made up of atoms, and since we are going to find a way to determine the relative weights of the *atoms* as well as of the *molecules*, it is important to adopt a final standard for molecular weights that will be suitable for both molecules and atoms. Thus, if it should turn out that the molecules of oxygen gas and hydrogen gas are not single atoms, *but are each made up of two atoms*, then the standard of 16 for the oxygen molecule would give us 8 for the oxygen atom and 0.5 for the hydrogen atom, and *it would be better to adopt 32 for the oxygen molecule so as to have the hydrogen atom at least 1.*

**Two atoms in the oxygen molecule.** It is clear that if molecules of compounds consist of two or more atoms, the molecules of elementary gases such as oxygen or hydrogen may either be single atoms or be composed of two or more atoms of the same kind. That the molecules of both oxygen and hydrogen consist of at least two atoms can be shown as follows:

When oxygen and hydrogen combine to form steam, we have the volume relations shown in the equation (p. 79)



Let us suppose that the 1 volume of oxygen contains 100 molecules. Then the 2 volumes of steam must contain 200 molecules (Avogadro's principle). But each of these 200 molecules must contain *at least* one atom of oxygen, or 200 in all, and these 200 atoms came from 100 molecules of oxygen. Consequently each molecule of oxygen must contain *at least* 2 atoms. Similar reasoning shows that the molecules of hydrogen also must contain at least 2 atoms.

Evidently we have merely shown that there are *at least* 2 atoms in these molecules. There might be more than that,

so far as our reasoning goes, but there is no evidence that points that way, and so we assume that there are 2 only. To retain 16 for the atom of oxygen (and a little above unity for that of hydrogen) *we will now adopt oxygen as 32 as the final standard for molecular and atomic weights*, and measure all others by this standard.

**Molecular weights from the weight of 22.4 liters.** Having adopted the arbitrary value oxygen = 32 as our standard, let us calculate the volume occupied by 32 grams of oxygen gas. Since 1 liter (of oxygen) weighs 1.429 g., the volume occupied by 32 g. will be  $\frac{32}{1.429}$ , or 22.4 liters. If we make a vessel that holds exactly 22.4 liters and fill it with oxygen, it will hold as many grams of oxygen (32 g.) as there are

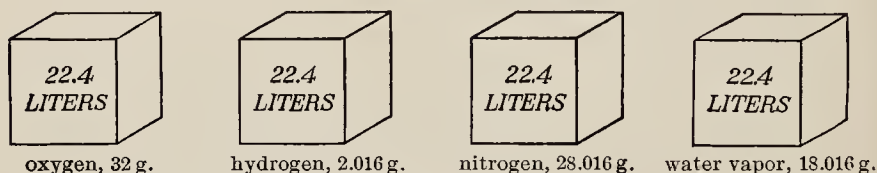


FIG. 46. The weight of 22.4 liters of various gases

units in the molecular weight of oxygen (32). If we now replace the oxygen with nitrogen, the same number of molecules will be present as before (Avogadro's principle), and experiment shows that the weight is 28.016 g. But these two numbers, 32 and 28.016, are the relative weights of an equal number of molecules, so that the nitrogen molecule weighs 28.016 as compared with the oxygen molecule taken as 32. In like manner the weight of 22.4 liters of *any* gas will give its molecular weight referred to oxygen as 32 (Fig. 46), and we can say that *the number that expresses the weight of 22.4 liters of any gas is the same as the number which expresses the molecular weight of the gas referred to oxygen as 32.*

**Gram-molecular volume.** The volume 22.4 liters is an important unit in chemistry. We have just seen that the weight



in grams of this volume of any gas gives us the same figure as the one that expresses the molecular weight of the gas referred to oxygen as 32. For this reason *22.4 liters is called the gram-molecular volume of a gas*. Experiment has shown that in this volume of a gas under standard conditions there are  $6.06 \times 10^{23}$  molecules. This is sometimes called *Avogadro's number*.

It should be added that no gas expands or contracts *exactly* as the gas laws say it should. In particular, gases not far from their point of liquefaction are compressed more than the laws would indicate when the pressure is increased, and so have an abnormal number of molecules in a given volume. The gram-molecular volume (22.4 liters) and Avogadro's number are therefore *average* numbers, from which gases differ slightly, though as a rule not more than a few tenths of one per cent. This fact does not impair in any way the usefulness of these constants.

**Selection of the atomic weights from the combining weights.** It will now be easy to show how we can decide which one of the combining weights of an element is really its atomic weight, and the best way to do this is by an example. So let us suppose that we have found that the combining weights of nitrogen are 7.005, 14.01, and 21.015; the atomic weight is therefore one of these numbers.

We first obtain the weight of 22.4 liters of a number of gaseous compounds which we know to contain nitrogen. These weights are given in the first column of the following table:

GASEOUS COMPOUNDS	MOLECULAR WEIGHT (22.4 LITERS)	PERCENTAGE OF NITROGEN BY EXPERIMENT	PART OF MOLECULAR WEIGHT DUE TO NITROGEN
Nitrogen gas . . . . .	27.95	100.00	27.95
Nitrous oxide . . . . .	44.13	63.70	28.11
Nitric oxide . . . . .	30.00	46.74	14.02
Ammonia . . . . .	17.05	82.28	14.03
Nitric acid . . . . .	63.75	22.27	14.30
Cyanogen . . . . .	52.20	53.64	28.00

We next analyze each of these compounds to ascertain the percentage of nitrogen present, placing in the second column the values obtained. If we multiply the molecular weight of each compound by the percentage of nitrogen, *the product will be the portion of the molecular weight due to nitrogen* (third column). But since the molecules are made up of *atoms*, the part of a molecule due to nitrogen must represent the *sum of the weights of the nitrogen atoms present*. We notice that the numbers in the last column are either very near to 14 or to twice 14, and that none are near 7 or 21. If we examine a large number of nitrogen compounds in this way, it is reasonable to expect that we shall find some that contain only one atom; and since we find none that give a value of less than 14, we assume that 14 and not 7 or 21 or 28 represents the weight of a nitrogen atom.

**Accurate determination of atomic weights.** The weight of a given volume of a gas is difficult to determine with great precision, and we have seen that Avogadro's principle is only approximately true. Consequently the molecular weights of gases as determined by experiment are usually subject to an error of a few tenths of 1 per cent. The portion of nitrogen in 22.4 liters of the various gases is therefore subject to about the same error, as will be seen from the values in the table above. All that these figures tell us is that the true value is *very near* 14. The smallest *combining weight* can be very accurately determined by the analysis of any of these compounds, and is found to be 7.005. It is therefore evident that the *accurate* atomic weight is twice this value, namely, 14.01.

**Summary.** These, then, are the steps which must be taken to establish the atomic weight of an element:

1. Determine the combining weight accurately by analysis.
2. Determine the weight of 22.4 liters of a large number of gaseous compounds of the element and, by analysis, the part of the molecular weight due to the element. The smallest number so obtained will be the *approximate* atomic weight.

3. Multiply the smallest combining weight by the integer (1, 2, or 3) which will give a number close to the approximate atomic weight. The number so obtained will be the *precise* atomic weight.

**Molecular weights of the elements.** When we determine the weight of 22.4 liters of the various *elementary* gases, we reach some interesting conclusions. Experiment shows that the molecular weights of many of them, such as nitrogen, chlorine, and bromine, give values which are *twice the atomic weights*, so that in these cases the molecule contains two atoms, as we have found to be true with oxygen and hydrogen (p. 99). In the case of the metals, so far as their vapors have been studied, the molecular weight and the atomic weight are the same, *so that the molecules of a metal consist of a single atom*. The molecule of ozone, on the other hand, contains three atoms of oxygen, while the molecules of phosphorus and of arsenic contain four atoms of these elements.

**Other methods for obtaining molecular weights.** The method for obtaining molecular weights evidently applies to gases only, including liquids and solids which can be converted into gases under such conditions that the resulting vapors can be collected, measured, and weighed. It will be noticed that Avogadro's principle gives us this method *because it states conditions under which we are sure we are dealing with an equal number of molecules of two kinds of gases*. Two laws have been formulated which give us this same kind of information in regard to the relative number of molecules of dissolved substances in a given volume of a solvent, and methods for obtaining molecular weights can be based on these laws.

**Raoult's laws.** The two laws just referred to are known as Raoult's laws and may be stated as follows:

1. *When weights of compounds (or elements) which are proportional to their molecular weights are dissolved in a given weight of a solvent, the rise in the boiling point of the solvent is the same in each case.*

2. *When weights of compounds (or elements) which are proportional to their molecular weights are dissolved in a given weight of a solvent, the lowering of the freezing point of the solvent is the same in each case.*

These two laws apply to a very wide range of substances and to very different solvents, but they do not hold true in those cases in which the solution is a good conductor of electricity. The reason for this will be discussed in a later chapter.

**Molecular weights of dissolved substances.** The application of the laws of Raoult to the measurement of molecular weights is very simple and may be made clear by an illustration. The molecular weight of alcohol, obtained by converting it into a vapor and weighing 22.4 liters, is 46. We dissolve 46 grams of alcohol in a definite volume of water, say 1 liter, and observe how much the freezing point of the water is lowered. We then dissolve in 1 liter of water the substance whose molecular weight we wish to measure, and keep adding portions of it until we have added enough to lower the freezing point to the same extent as was produced by 46 g. of alcohol. Since the lowering is the same in both cases, equal numbers of molecules of the two substances have been dissolved; and since we used as many grams of alcohol as there are units in its molecular weight, the weight of the second substance will also be the same as its molecular weight. We can proceed in exactly the same way to measure molecular weights by the rise in the boiling point.

**Weight of a liter of a gas.** The weights of 1 liter of various gases as given throughout this book have been obtained by weighing the gases in question; from these weights we calculate the molecular weights of the gases. Conversely, if we happen to know the molecular weight of a gas, we can easily calculate back to the weight of 1 liter of that gas; for the figure that represents the molecular weight is also the actual weight in grams of 22.4 liters of the gas. Hence, to find the approximate weight in grams of 1 liter of any gas under standard conditions, divide its molecular weight by 22.4. This



will give merely the approximate weight of 1 liter, for 22.4 is the *average* gram-molecular volume of all gases. The figure will, however, be accurate enough for many purposes.

## EXERCISES

1. Report the important events in the life of Dalton (consult encyclopedia).

2. State all the laws mentioned in this chapter.

3. Calculate the weights of hydrogen that combine with 100 g. of oxygen to form water and hydrogen peroxide respectively. Are your results in accord with the law of multiple proportion?

4. (a) What is the derivation and meaning of the word *atom*? (Consult dictionary.) (b) Is the word a misnomer?

5. Why did Dalton make the assumption that the atoms of the same element all have exactly the same weight?

6. What is meant by the following terms: (a) atom of an element; (b) molecule of an element; (c) molecule of a compound?

7. Would it be logical to speak of an atom of a compound?

8. Calculate the molecular weights of hydrogen, oxygen, and hydrogen chloride from the weight of 1 liter of each of these gases (Appendix).

9. Carbon dioxide is one of the gases exhaled from our lungs. Calculate its molecular weight from the weight of 1 liter of the gas.

10. When sulfur burns in oxygen or air (p. 31) a gas known as *sulfur dioxide* forms. The molecular weight of sulfur dioxide is 64.06. (a) Calculate the weight of 1 liter of the gas. (b) Compare your result with that given in the Appendix.

11. The chief constituent of natural gas is a compound of carbon and hydrogen known as *methane*. Its molecular weight is 16.04. (a) Calculate the weight of 1 liter of the gas. (b) Compare your result with that given in the Appendix.

12. Sulfur dioxide contains 50.05 per cent of sulfur. One liter of the gas weighs 2.9236 g. Assuming that the molecule of the sulfur dioxide contains but one atom of sulfur, calculate the atomic weight of sulfur from the above data. (*Suggestion.* First calculate the molecular weight of the gas; then determine how much of this weight is sulfur.)

13. Carbon dioxide (see exercise 9, above) contains 72.72 per cent of oxygen. Assuming that the molecule of the gas contains two atoms of oxygen, calculate the atomic weight of oxygen.

22.4 + 16.04

## CHAPTER IX

### FORMULAS; EQUATIONS; SOLUTION OF PROBLEMS

**Percentage composition.** Just as we can determine the composition of water with great accuracy, so, by similar means, we can determine the composition of other compounds. Having analyzed a given compound, we usually express its composition in percentages, or in the parts of each element present in 100 parts of the compound. Thus, we have seen that water consists of 88.81 per cent of oxygen and 11.19 per cent of hydrogen.

**Atomic composition; formulas.** We may express composition in an entirely different way, namely, by indicating the *number* and *kind* of atoms in a molecule of a compound. For example, if we write the symbol of mercury and of oxygen together, as  $\text{HgO}$ , we may take this to mean that a molecule of mercuric oxide is composed of an atom of mercury and one of oxygen. Similarly,  $\text{Hg}_2\text{O}$  would indicate that the molecule is composed of two atoms of mercury and one of oxygen;  $\text{HgO}_2$ , that it is composed of one atom of mercury and two of oxygen. *A group of atomic symbols representing the composition of a molecule of a compound is called a formula.* Of course there can be only one correct formula for a given compound, and we shall soon see that there are methods by which we can decide that mercuric oxide is  $\text{HgO}$ .

**Formulas deduced from molecular weights.** If we can determine the molecular weight of a compound by experiment (and this is generally possible), we can calculate the formula in a very simple way. Thus, suppose we know that the molecular weight of water vapor is approximately 18. This represents

the sum of all the atomic weights in the molecule. Multiplying 18 by the percentage of hydrogen (11.19) gives us 2 as the sum of the hydrogen atoms present, or 2 atoms. Multiplying 18 by 88.81 gives as the sum of the oxygen atoms 15.99, or almost exactly 16, or 1 atom. This gives us at once the formula  $H_2O$ .

**Formula of alcohol.** As a second example let us deduce the formula of alcohol. Analysis shows that this compound consists of 52.17 per cent of carbon; 34.79 per cent of oxygen; and 13.13 per cent of hydrogen. Its molecular weight as a vapor is found to be about 46.

$$(46 \times 52.17) \div 100 = 23.99 = 2 \text{ atoms of carbon}$$

$$(46 \times 34.79) \div 100 = 16 = 1 \text{ atom of oxygen}$$

$$(46 \times 13.13) \div 100 = 6.039 = 6 \text{ atoms of hydrogen}$$

The formula for alcohol is therefore  $C_2H_6O$ .

**Calculation of formulas from percentages.** If we are unable to determine the molecular weight of a compound by experiment, we can still deduce its *simplest* formula from its percentage composition; though we cannot be sure that some multiple of it is not the *real* formula. The way in which we deduce this simplest formula can best be made clear by an example.

We have seen that water consists of 88.81 per cent of oxygen and 11.19 per cent of hydrogen. If we divide the percentage of the oxygen in water by the atomic weight of oxygen (16), the quotient (5.55) will be the *relative number of oxygen atoms in 100 parts of water*. In like manner, if we divide the percentage of hydrogen (11.19) by the atomic weight of the element (1.008), the quotient (11.10) will express the *relative number of hydrogen atoms in 100 parts of water*. The two numbers, 5.55 and 11.10, therefore represent the *ratio between the number of oxygen and hydrogen atoms in 100 g. of water*. To reduce the ratio to its simplest terms we divide the two numbers by the smaller one:

$$11.10 \div 5.55 = 2; 5.55 \div 5.55 = 1$$

The ratio of hydrogen atoms to oxygen atoms in a molecule of water is therefore 2 : 1, and the *simplest* formula of water is  $\text{H}_2\text{O}$ .

**Derivation of the formula of potassium chlorate.** Let us take another example. Potassium chlorate, when analyzed in the laboratory, is found to be as follows : potassium, 31.9 per cent; chlorine, 28.9 per cent; oxygen, 39.2 per cent. Now, proceeding as in the case of water, we get the following results :

$$31.9 \div 39.10 = 0.816 = \text{relative number of atoms of K in 100 g.}$$

$$28.9 \div 35.457 = 0.815 = \text{relative number of atoms of Cl in 100 g.}$$

$$39.2 \div 16.00 = 2.450 = \text{relative number of atoms of O in 100 g.}$$

Dividing the three quotients by the smallest (0.815), we get the integers 1, 1, 3. The simplest formula of potassium chlorate is therefore  $\text{KClO}_3$ , and its real formula is either  $\text{KClO}_3$  or some multiple of this. (Since analyses are always slightly inaccurate, the ratios found will often differ slightly from whole numbers, but the difference is so slight as to leave no doubt as to what the integer really is.)

**Deduction of percentage composition of compounds from formulas.** From the formula of a compound we can easily go back to the percentages from which it was calculated. Thus, if the molecule of water weighs 18.016 and contains one oxygen atom of weight 16, the fraction of its weight due to oxygen is  $\frac{16}{18.016} = 88.81$  per cent. The fraction due to hydrogen is  $\frac{2.016}{18.016} = 11.19$  per cent.

Let us take another example; namely, hydrogen sulfate. Its formula is  $\text{H}_2\text{SO}_4$ ; hence its molecular weight is the sum of 2 times the atomic weight of hydrogen ( $2 \times 1.008$ ), plus the atomic weight of sulfur (32.06), plus 4 times the atomic weight of oxygen ( $4 \times 16$ ), or 98.076.

$$\text{Percentage of hydrogen} = \frac{2.016}{98.076} = 2.05$$

$$\text{Percentage of sulfur} = \frac{32.06}{98.076} = 32.70$$

$$\text{Percentage of oxygen} = \frac{64}{98.076} = 65.25$$



**Facts expressed by formulas.** From what has been said it will be seen that formulas are used to express several distinct facts :

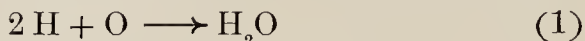
1. *Atomic composition of molecules.* A formula shows the number and kinds of atoms in a molecule of a compound. The formula  $\text{H}_2\text{O}$  states that a molecule of water is composed of two atoms of hydrogen and one of oxygen. The formula of hydrogen sulfate ( $\text{H}_2\text{SO}_4$ ) shows that its molecule consists of two atoms of hydrogen, one of sulfur, and four of oxygen.

2. *Molecular weights of compounds.* Since each atom has its own weight, the sum of all the atoms in a molecule must be the weight of the molecule itself relative to the oxygen atom taken as 16. The relative weight of the molecule of water is therefore  $(2 \times 1.008) + 16 = 18.016$ . The relative weight of the molecule of hydrogen sulfate ( $\text{H}_2\text{SO}_4$ ) is  $(2 \times 1.008) + 32.06 + (4 \times 16) = 98.076$ .

3. *Composition of compounds.* For practical purposes we deal with pounds or with grams of a substance, not with atoms and molecules. Now, since the numbers 18.016, 16, and 2.016 represent the ratio by weight between a molecule of water and the oxygen and hydrogen of which it is composed, the same ratios must hold between any weight of water we may choose and the oxygen and hydrogen in this weight of water; for any quantity of water is made up of molecules of water. Evidently in 18.016 lb. of water there will be 16 lb. of oxygen and 2.016 lb. of hydrogen, and in 18.016 g. there will be 16 g. of oxygen and 2.016 g. of hydrogen.

**Gram-molecular weights.** For practical purposes we may allow the symbol H to stand for 1.008 g. of hydrogen, the symbol O for 16 g. of oxygen, and the formula  $\text{H}_2\text{O}$  for 18.016 g. of water. The weight in grams of an element, corresponding to its atomic weight, is called a *gram-atomic weight*. The weight in grams of an element or of a compound, corresponding to its molecular weight, is called a *gram-molecular weight*.

**Equations.** Having devised a convenient way of expressing the composition of compounds, not in percentages but in formulas, we make use of *equations* to express chemical transformations, using an arrow in place of an equality sign. For example, the equation

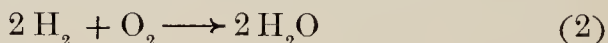


is a concise method of stating two distinct facts.

1. *Qualitatively*, it states that water is formed by the union of hydrogen and oxygen.

2. *Quantitatively*, it tells us that 2 gram-atomic weights of hydrogen (2.016 g.) combine with 1 gram-atomic weight of oxygen (16 g.) to form 1 gram-molecular weight of water (18.016 g.).

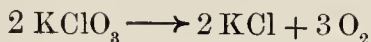
**Molecular equations.** Since a formula expresses the composition of a molecule, and since experiment has shown that a molecule of oxygen and one of hydrogen each contain two atoms (p. 99), the formulas of these gases are written  $\text{O}_2$  and  $\text{H}_2$  rather than  $2 \text{O}$  or  $2 \text{H}$ , which would simply represent two atoms *not combined*. If we wish our equation to state these additional facts, we shall have to change it to the form



This is called a *molecular equation*, and it will be seen that it expresses the same ratios by weight as does equation (1). It expresses the additional fact that 2 molecules of hydrogen combine with 1 molecule of oxygen to form 2 molecules of water, and this for some purposes makes it a more useful equation. In this text we shall ordinarily use the molecular equations, although we may sometimes use the simple form if we wish to express only ratios.

**Decomposition of potassium chlorate.** Let us take another example of the meaning of an equation. It will be remembered that oxygen was prepared by heating potassium chlorate, which has the formula  $\text{KClO}_3$ . When heated, this compound decomposes into oxygen and

a compound called potassium chloride, whose formula is  $\text{KCl}$ . The decomposition is represented by the equation



This equation states the following facts:

1. *Qualitatively*, potassium chlorate decomposes into potassium chloride and oxygen.

2. *Quantitatively*, 2 gram-molecular weights of potassium chlorate ( $2 \times 122.557$  g.) decompose into 2 gram-molecular weights of potassium chloride ( $2 \times 74.557$  g.) and 3 gram-molecular weights of oxygen ( $3 \times 32$  g.). The number before a formula applies to the formula as a whole, while the subscript number applies only to the symbol which it follows.

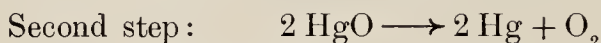
3. *Molecularly*, 2 molecules of potassium chlorate decompose into 2 molecules of potassium chloride and 3 of oxygen.

**Steps in writing an equation.** *We must keep in mind that chemical equations simply express facts deduced from experiments.* In other words, we cannot find out by equation-writing what the formula of a compound is or what changes the compound undergoes, but, *having found out these facts*, we can express them by an equation. In writing an equation the first step consists in writing, on the left of the arrow ( $\longrightarrow$ ), the formulas (or symbols) of the substances entering into the reaction, and on the right the formulas (or symbols) of the substances formed. Thus, having learned that the formula of mercuric oxide is  $\text{HgO}$ , that it decomposes into mercury and oxygen on heating, and that the oxygen molecule is  $\text{O}_2$ , while the mercury atoms remain single (p. 103), we express these facts as follows:



The second and final step consists in *balancing the equation*; that is, we must modify our equation (if necessary) so that there will be just as many atoms of each element on one side of the equation as on the other. Thus, in the above equation we have two atoms of oxygen (or 1 molecule) on one side of the equation. To get this we must take  $2 \text{HgO}$ , and this will give

us 2 Hg as well as  $O_2$ ; hence we write the completed equation, keeping in mind also the fact that the molecules and atoms of metals are, as a rule, identical (p. 103):

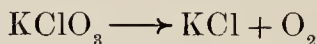


**Equations of reactions so far studied.** Let us now put into the form of equations the reactions studied up to this point, writing both steps. *Remember that the complete equation in each case is the correct one; the first is written simply as an aid in formulating the completed equation.*

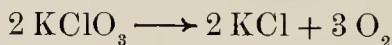
**1. Preparation of oxygen:**

(a) From potassium chlorate:

First step:

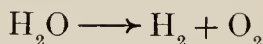


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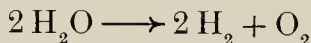


(b) From the electrolysis of water:

First step:

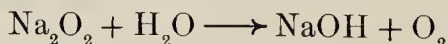


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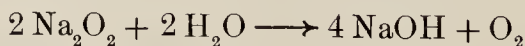


(c) From sodium peroxide and water:

First step:



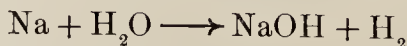
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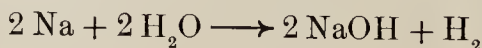
**2. Preparation of hydrogen:**

(a) From sodium and water:

First step:



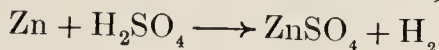
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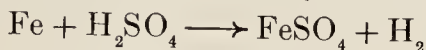
(b) From zinc and sulfuric acid:

First step and complete (identical):



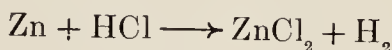
(c) From iron and sulfuric acid:

First step and complete (identical):

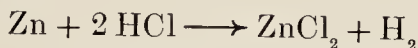


(d) From zinc and hydrochloric acid:

First step:

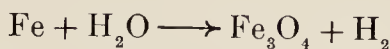


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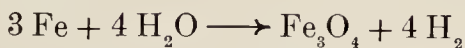


(e) From iron and steam:

First step:

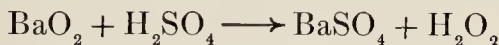


Complete:



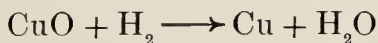
### 3. *Preparation of hydrogen peroxide:*

First step and complete (identical):

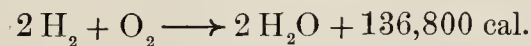


### 4. *Reducing copper oxide by hydrogen:*

First step and complete (identical):



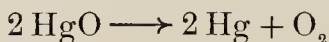
**Representation of the heat of reaction.** We can also employ chemical equations to express the heat given off or absorbed during chemical action. The equation



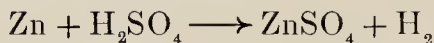
states the fact that when 4.032 g. of hydrogen combines with 32 g. of oxygen, forming 36.032 g. of water, heat is given off to the extent of 136,800 cal. Evidently when 1 gram-molecular

weight (18.016 g.) of water is formed, 68,400 cal. is given off, and this is called the *heat of formation* of water.

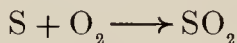
**Conditions of a reaction not indicated by equations.** Equations merely state the composition of the substances taking part in the reaction and the weights of each one involved, together with the energy change measured as heat. They do not tell the conditions under which the reaction will take place. For example, the equation



does not tell us that it is necessary to keep heating the mercuric oxide at a moderately high temperature in order to effect its decomposition. The equation



in no way indicates that the hydrogen sulfate must be dissolved in water before it will act upon zinc. The equation



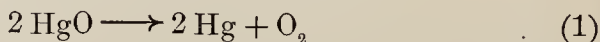
does not indicate that no perceptible action takes place unless the sulfur is first heated, but that when once started it goes on of its own accord and with a bright flame.

It will therefore be necessary to pay close attention to the details of the conditions under which a given reaction occurs, as well as to the statement of the equation itself.

**Problems based on equations.** Since an equation is a statement of the weights of materials which take part in a reaction, when the equation has once been established by experiment we can use it in calculating the various weights. A few examples will show how this may be done.

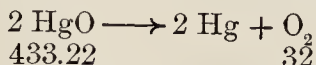
1. How many grams of oxygen are evolved on heating 100 g. of mercuric oxide?

First write the equation for the reaction involved:



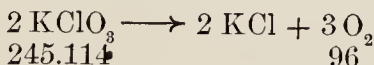
Next determine the *relative* weights of the amounts of the different substances involved in the reaction. The atomic weights of

mercury and oxygen are respectively 200.61 and 16 (see table on back cover). Hence the relative weight of the  $2 \text{ HgO}$  equals  $2(200.61 + 16)$ , or 433.22. Similarly, the relative weight of the oxygen evolved, namely,  $\text{O}_2$ , equals  $2 \times 16$ , or 32. It is convenient now to write these numbers under the formulas in equation (1). This then becomes



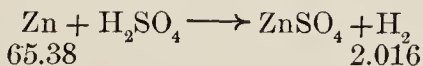
These numbers indicate that 433.22 units by weight (in this case grams) of mercuric oxide will, on heating, evolve 32 units by weight of oxygen; hence 1 g. of mercuric oxide will give  $\frac{32}{433.22}$  g. of oxygen, and 100 g. will give  $100 \times \frac{32}{433.22}$ , or 7.38 g.

2. I wish to prepare 100 g. of oxygen; using potassium chlorate as a source of the oxygen. How many grams of the chlorate will be required?



The figures tell us that 245.114 g. of potassium chlorate will yield 96 g. of oxygen; hence to prepare 1 g. of oxygen we must use  $\frac{245.114}{96}$  g. of potassium chlorate, and to prepare 100 g. we must have  $\frac{245.114}{96} \times 100 = 255.33$  g.

3. How many grams of zinc must be dissolved in sulfuric acid to produce 10 g. of hydrogen?



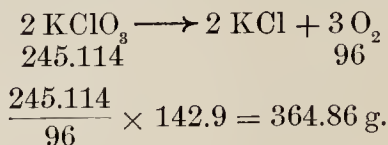
To obtain 2.016 g. of hydrogen we must use 65.38 g. of zinc. Hence, to obtain 1 g. of hydrogen  $\frac{65.38}{2.016}$  g. of zinc is required, and to obtain 10 g. we must take 10 times as much; namely,  $\frac{65.38}{2.016} \times 10 = 324.30$ .

It must be remembered that the equations show relations by *weight*, not by volume; hence in problems involving volumes of gases it will be necessary first to find the weights of the gases. The table in the Appendix gives the weight of 1 liter of each of the common gases, measured under standard conditions. The following problem will illustrate the method:

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4. How many grams of potassium chlorate are necessary to prepare 100 liters of oxygen?

Since 1 liter of oxygen weighs 1.429 g., 100 liters will weigh 142.9 g.



It will be recalled that in Chapters III and IV we solved a number of problems of the same kind as those solved above, but in the earlier chapters these problems were solved by referring to the percentage composition of the compounds. Having now learned the significance of formulas and equations, we find it much simpler to solve problems of this kind by reference to the formulas and equations involved in the problem.

In working out such problems, do not carry divisions beyond the second decimal place. Having completed a problem, look to see if the result is reasonable.

### EXERCISES

1. A compound was found, on analysis, to contain 5.93 per cent of hydrogen and 94.07 per cent of oxygen. Experiments proved its molecular weight to be approximately 34. Calculate the formula of the compound.

2. A compound analyzed in the laboratory was found to contain 2.76 per cent of hydrogen and 97.24 per cent of chlorine. Its molecular weight was found to be approximately 36. Calculate its formula.

3. Common salt has a molecular weight of approximately 58 and contains 39.34 per cent of sodium and 60.65 per cent of chlorine. Calculate its formula.

4. Ordinary saltpeter has a molecular weight of approximately 101 and contains 38.67 per cent of potassium, 13.88 per cent of nitrogen, and 47.45 per cent of oxygen. Calculate its formula.

5. A compound was found, on analysis, to have the following composition: iron, 36.76 per cent; sulfur, 21.10 per cent; and oxygen, 42.13 per cent. Calculate its simplest formula.

6. A compound containing calcium, sulfur, and oxygen gave, on analysis, 29.40 per cent of calcium and 23.56 per cent of sulfur. Calculate its simplest formula.

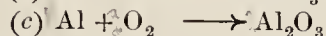


7. Calculate the simplest formula of the compound which has the following composition: potassium, 38.67 per cent; nitrogen, 13.88 per cent; and oxygen, 47.45 per cent.

8. Calculate the percentage composition of the following compounds from the formulas as given: (a) potassium chlorate ( $\text{KClO}_3$ ); (b) hydrogen sulfate ( $\text{H}_2\text{SO}_4$ ); (c) water ( $\text{H}_2\text{O}$ ); (d) saltpeter ( $\text{KNO}_3$ ); (e) baking soda ( $\text{NaHCO}_3$ ).

9. State all the facts expressed by the formulas  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{CaO}_2\text{H}_2$ ,  $\text{H}_3\text{PO}_4$ .

10. Balance the following equations:



11. It is required to prepare 30 g. of oxygen by heating mercuric oxide. What weight of the oxide must be heated?

12. What weight of hydrogen will be obtained from the action of sulfuric acid on 100 g. of zinc? What will be its volume under standard conditions?

13. A given volume of oxygen standing over water at  $20^\circ$  and 745 mm. measures 10 liters. (a) What would be its volume under standard conditions? (b) What is its weight? (c) What weight of potassium chlorate would be required to prepare this amount of oxygen?

14. 100 cc. of sulfuric acid containing 20 g. of hydrogen sulfate ( $\text{H}_2\text{SO}_4$ ) was added to 10 g. of zinc. Calculate the weight of hydrogen evolved.

15. When hydrogen is liberated by the action of zinc on sulfuric acid, what weight of zinc sulfate is formed for each gram of hydrogen liberated?

16. If you had 10 g. of iron with which to prepare hydrogen, should you heat it with steam or act upon it with sulfuric acid in order to obtain the maximum quantity of hydrogen?

17. What weight of potassium chlorate is necessary to furnish sufficient oxygen to fill four 200-cubic-centimeter bottles in your laboratory (the gas to be collected over water)?

18. Calculate the weight of the compounds necessary for preparing 10 kg. of the common medicinal hydrogen peroxide.

19. A bottle containing 1 kg. of medicinal hydrogen peroxide was set aside until the peroxide was completely decomposed into water and

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oxygen. (a) Calculate the volume of the oxygen evolved. (b) Calculate the weight of the water left in the bottle.

20. 10 g. of zinc was used in the preparation of hydrogen. What weight of iron will be required to prepare an equal volume of the gas?

21. 1 kg. of potassium chlorate was heated until all the oxygen was evolved. Calculate the weight of the potassium chloride left.

22. 100 g. of water in the form of steam is passed over heated iron. What weight of hydrogen results?

23. (a) What volume of hydrogen is necessary to reduce 100 g. of copper oxide? (b) What weight of water would be formed in the process?

24. 100 g. of sodium reacts with water to liberate hydrogen. What volume of hydrogen is liberated?

25. 1000 liters of hydrogen is prepared by the action of sulfuric acid on iron. What weight of iron sulfate ( $\text{FeSO}_4$ ) is formed in the process?

26. A certain Zeppelin airship has a capacity of 20,000 cubic meters. Supposing that the hydrogen used in inflating this is made by the action of sulfuric acid on iron, calculate the weight of hydrogen sulfate and iron necessary to inflate this airship at  $20^\circ$  and 740 mm.

## CHAPTER X

### THE THREE STATES OF MATTER

**Gases, liquids, and solids.** We have found that water exists in three very different states: namely, as gas, as liquid, and as solid. In a general way these three states may be described by saying that a gas (or vapor) is that form of matter that tends to distribute itself uniformly throughout the space in which it is placed. A liquid collects in the bottom of the containing vessel; it has no characteristic form of its own, but takes the shape of the vessel in which it is placed. A solid retains its own form irrespective of the shape of the vessel. Most substances can be obtained in all these states.

**Evaporation.** When a liquid such as water is placed in an open vessel, it gradually passes into the air in gaseous form, or *evaporates*. In a confined space, as in a partly filled bottle, evaporation takes place until the air above the liquid contains a definite percentage of vapor, or becomes *saturated* with the vapor. The process of evaporation does not really cease when saturation is reached, but the rate at which the vapor is formed from the liquid is just balanced by the rate at which the vapor condenses to form the liquid. Saturation is therefore a balance between these two rates.

If the liquid is now warmed, the rate of evaporation is increased. A new balance is reached at this higher temperature, with a higher percentage of vapor present in the air than there was before. The vapor formed from the liquid is a gas and, like any other gas, exerts a pressure upon the walls of the containing vessel and upon the surface of the liquid. This pressure, as stated in a previous chapter (p. 60), is spoken of as the *vapor pressure* of the liquid.

**Relative humidity.** The phrase *relative humidity* is familiar in the government weather reports. By the humidity at a given time is meant the percentage of water vapor in the air as compared with the percentage present at saturation at the same temperature. To be comfortable, air should be about 70 per cent saturated.

**Boiling point.** While a liquid is being heated, a part of the heat energy added to it is used in raising its temperature by increasing the motion of the molecules of the liquid; a part is absorbed in converting the liquid into vapor against the attraction of the molecules that tends to hold it together as a liquid. The formation of this vapor is opposed by the pressure of the atmosphere. When the pressure of the vapor just above the liquid becomes great enough to overcome the pressure of the atmosphere, the air is pushed back by the vapor. All the heat energy supplied to the liquid is now used in changing the liquid into vapor and in the mechanical work of pushing back the atmosphere, and the temperature ceases to rise. If the opposing atmospheric pressure is increased, the liquid must be heated to a higher temperature before its vapor pressure will exceed the higher pressure. The temperature at which the pressure of the vapor just exceeds the pressure of the atmosphere is called the *boiling point* of the liquid. It will be seen that the point changes with the pressure. Under a pressure of 760 mm. water boils at  $100^{\circ}$ ; under a pressure of 525.5 mm. it boils at  $90^{\circ}$ .

**Heat of vaporization and of condensation.** The quantity of heat required to change 1 g. of a liquid *at its boiling point* into 1 g. of vapor at the same temperature is called the *heat of vaporization*. For water this is unusually large and amounts to 539 cal. If a gas is maintained at a pressure of 760 mm. and is gradually cooled, condensation into a liquid will begin when the boiling point is reached. During condensation the temperature remains constant and the quantity of heat given out in the process (*heat of condensation*) is exactly equal to



the heat of vaporization. Since the heat given out tends to check the process, condensation is not rapid unless some method is devised for absorbing the heat.

**Critical point.** If a liquid is sealed within a tube *A* (Fig. 47) from which all air has been withdrawn, the lower end of the tube will be filled with liquid and the upper end will contain vapor. If the liquid is now heated by a burner, it cannot boil, for the pressure of its vapor cannot overcome the opposing pressure and escape. As the heating progresses, more and more of the liquid is vaporized. The density of the remaining liquid diminishes, and the density of the vapor increases. Evidently at some temperature the two will become identical, and the boundary line between them, *B* (the *meniscus*), will fade out. The temperature at which this occurs is called the *critical temperature*, and the pressure exerted by the vapor at this temperature is the *critical pressure*. Above this temperature the greatest conceivable pressure will not liquefy the gas but will merely compress it. Before any gas can be liquefied it must first be cooled below its critical temperature. The critical points of a few gases are given in the following table:

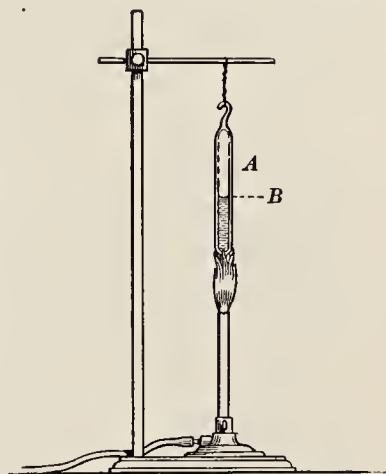


FIG. 47. Drawing illustrating the critical temperature of a liquid

TABLE OF CRITICAL POINTS

	BOILING POINT	CRITICAL TEMPERATURE	CRITICAL PRESSURE
Hydrogen . . . . .	- 252.7°	- 241.0°	15.0 atmospheres
Nitrogen . . . . .	- 195.8°	- 146.0°	33.0 atmospheres
Oxygen . . . . .	- 183.0°	- 118.0°	50.0 atmospheres
Water . . . . .	+ 100.0°	+ 360.0°	195.0 atmospheres

**Methods of liquefaction of gases.** The earliest systematic efforts at liquefaction of gases were those of the English scientist Faraday, beginning about 1823. He relied upon the effect of pressure together with moderate cooling, most of his experiments being carried out in the following way: A quantity of solid material which, when heated, would liberate a considerable quantity of the gas to be liquefied, was placed

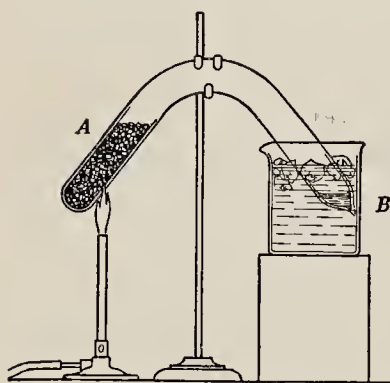


FIG. 48. Drawing illustrating Faraday's method of liquefying gases

in one end of a bent tube. The other end was sealed and the tube arranged as shown in Fig. 48, *A* being the solid material and *B* a bath of ice water. Upon heating, the gas is given off in a confined space and, being under great pressure, liquefies in the cold portion of the tube. In this general way Faraday liquefied a number of gases, such as ammonia and carbon dioxide.

Later experimenters made use of much lower temperatures.

These low temperatures were secured by taking advantage of the heat of vaporization of low-boiling liquids. When a quantity of any gas, such as sulfur dioxide, is liquefied by pressure, cooled, and then allowed to boil away under the pressure of the atmosphere or in a partial vacuum, the temperature of the liquid falls to its boiling point under that pressure. The very cold, boiling liquid may be used as a bath to cool some other gas below its critical temperature, when it may in turn be liquefied by pressure. By employing such a process Cailletet, in 1877, first liquefied oxygen.

Since 1895 purely mechanical methods have been employed in liquefying such gases as air. Machines constructed for this purpose depend for their efficiency upon the cooling effect produced when a highly compressed gas is allowed to expand

freely. When a gas is compressed, heat is liberated; and when it is allowed to expand, heat is absorbed. The two quantities of heat are not quite equal, for when the gas is compressed, the attraction of the gas particles for each other *assists* the external pressure, but the same forces in the compressed gas tend to *prevent* expansion. Both these effects are in the same direction, and this causes the heat absorbed in expansion to be slightly more than that given off during compression.

When a gas is alternately compressed and expanded, its temperature steadily falls to the point of liquefaction.

**The Hampson liquefier.** The essential features of the Hampson type of liquefier are shown in Fig. 49. The air, compressed to about 200 atmospheres by a compressor engine and cooled by running cold water, enters the liquefier at *A*. The tube *A* divides into three or four small copper tubes wound in spirals of many turns so as to fill the cylindrical housing of the liquefier as full as possible with a mesh of tubes having a very large surface. These small tubes reunite into the tube *B*, which is provided with a needle valve at *C* through which the compressed air escapes and expands to atmospheric pressure. In doing so it becomes very cold and is led back over the mesh of spiral tubes, cooling them and their contents of compressed air, and finally leaves the liquefier at *D*. It then goes to the compressor and is once more compressed. During the process the air within the small tubes becomes colder and colder until some of it drops through the needle valve as a liquid and collects in the cup *E*, from which it can be drawn off from time to time through the tube *F*.

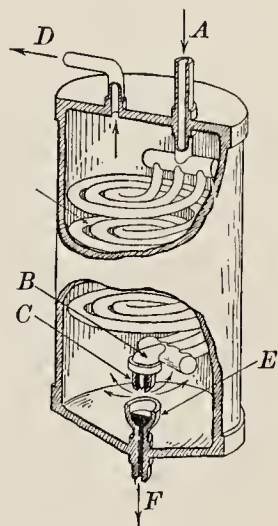


FIG. 49. The essential features of the Hampson liquefier

**Dewar flasks; thermos bottles.** Liquid air may be kept for some hours in a special form of flask, devised by the Scottish scientist Dewar, known as a *Dewar flask*. This consists of two

concentric vessels (Fig. 50) of any convenient shape. These are joined together at the upper rim only, and the space between them is exhausted by an air pump. The vacuum serves as the best possible insulator to prevent heat conduction. The surface of the outer flask is often silvered in order to reflect the external heat and thus prevent its absorption. The vessels known as *thermos bottles* (Fig. 51) are constructed on the same plan and are very effective for keeping liquids either hot or cold for several hours.

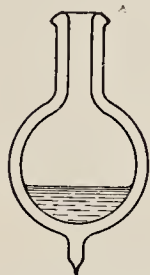


FIG. 50. A Dewar flask for holding liquid air

**Surface tension.** The molecules of a liquid are very close together, and each molecule very strongly attracts every other molecule close to it. A molecule *A* (Fig. 52) in the body of a liquid may be regarded as affected by all the molecules within a small circumscribed sphere, and the attraction in one direction is balanced by an equal attraction in the opposite direction. This is not true of a molecule *B* in or near the surface of the liquid. All the particles within the indicated hemisphere pull it back toward the body of the liquid, and there is no balancing force to pull it forward. The condition of the surface of the liquid is therefore one of strain, or ten-

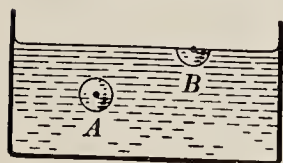


FIG. 52. Drawing illustrating surface tension

sion, and this is called *surface tension*. One result of this surface tension is that liquids evaporate slowly. Only the fast-moving molecules can break clear of the attractive forces at the surface. A second result is that surface tension tends to contract the surface to the smallest possible area. Small quantities of a liquid are drawn into spherical drops, and it takes the expenditure of



FIG. 51. A thermos bottle



work to increase the surface of a liquid, because this involves bringing into the surface a vast number of molecules from their balanced state in the interior of the liquid.

**Solid bodies.** When a liquid substance is cooled, it becomes less and less fluid. At a sufficiently low temperature all liquids become rigid, and we call this form a *solid*. As a rule the change from liquid to solid is sudden. At some definite temperature crystals (p. 127) begin to form and the temperature of the liquid comes to a perfectly definite value called the *freezing point*, and this remains unchanged until all the liquid has solidified. For example, water solidifies, or freezes, at  $0^{\circ}$ . Solids formed in this way are always *crystalline*. Less frequently there is no definite point of solidification, the changes from the liquid state into that of a rigid body being very gradual. Glasses, glazes, glue, tar, and gums are examples of such materials. These are sometimes called *amorphous solids*, to distinguish them from crystalline solids, but it is better to consider them as still liquid but so lacking in fluid properties that they are as rigid as crystalline solids.

**Freezing point.** When a crystallizable liquid, such as water, is cooled, it does not always *begin* to crystallize at its freezing point. Indeed, liquid water has been cooled to  $-90^{\circ}$  without freezing. A liquid below its freezing point is said to be *undercooled*. If a crystal once forms, or if one is dropped into the undercooled liquid, solidification at once begins, heat is given out in the process, and the temperature rises to the true freezing point and remains there as long as any liquid is present. The freezing point is best defined as *the temperature at which both solid and liquid will remain in contact with each other without change of temperature*.

**Heat of solidification.** The heat given out when 1 g. of a liquid at its freezing point solidifies to 1 g. of solid is called the *heat of solidification*. For water this amounts to 80 cal. If it were not for this liberation of heat, which opposes solidification, ponds would freeze solid in the winter as soon as



crystallization had begun. Liquids which do not have definite freezing points have no heat of solidification; this shows that the rigid bodies formed from them are fundamentally different from crystalline solids.

**Melting point.** If a crystalline solid is slowly heated, its temperature steadily rises to its freezing point and the change to the liquid then begins; and it has not been found possible to raise the temperature of the solid beyond this point. The melting point and the freezing point are therefore at the same temperature. To convert 1 g. of a solid at its melting point into a liquid at the same temperature absorbs the same quantity of heat as was liberated during solidification. This is called the *heat of fusion*. Amorphous rigid bodies have no definite melting point or heat of fusion.

**The manufacture of ice.** The manufacture of ice is based on the principle that in the process of vaporizing a liquid a great deal of heat is absorbed (heat of vaporization). If the process is so conducted that the liquid in vaporizing absorbs this heat from water, the temperature of the water may be brought to the freezing point, and by still further absorption of heat the water may be frozen. It will be recalled that for every gram of water at  $0^{\circ}$  frozen into ice 80 cal. is evolved, and this heat must be absorbed. The liquid chosen to be vaporized must readily pass into a vapor at  $0^{\circ}$  if the pressure upon it is lowered, and it should have as great a heat of vaporization as possible. Liquid ammonia (heat of vaporization, 330 cal.) is the one most frequently used.

**Details of the process.** The general method used in the manufacture of artificial ice may be understood by reference to Fig. 53. Ammonia, a gaseous compound formed when soft coal is heated in the absence of air (p. 219), is liquefied by means of a compressor pump *B* and led into the pipes *A*. The heat of condensation is absorbed by water flowing over the pipes. These pipes lead into coils in a large tank *C*, nearly filled with brine, prepared by dissolving calcium chloride in water. Such a brine may be cooled

quite a little below zero without freezing. By means of an expansion valve *E* the pressure upon the liquid ammonia is diminished as it enters the coils, and the heat absorbed by the rapid evaporation of the liquid lowers the temperature of the brine below  $0^{\circ}$ . Metal vessels *D, D, D*, filled with pure water, are lowered into the cold brine and left until the water in them is frozen into cakes of

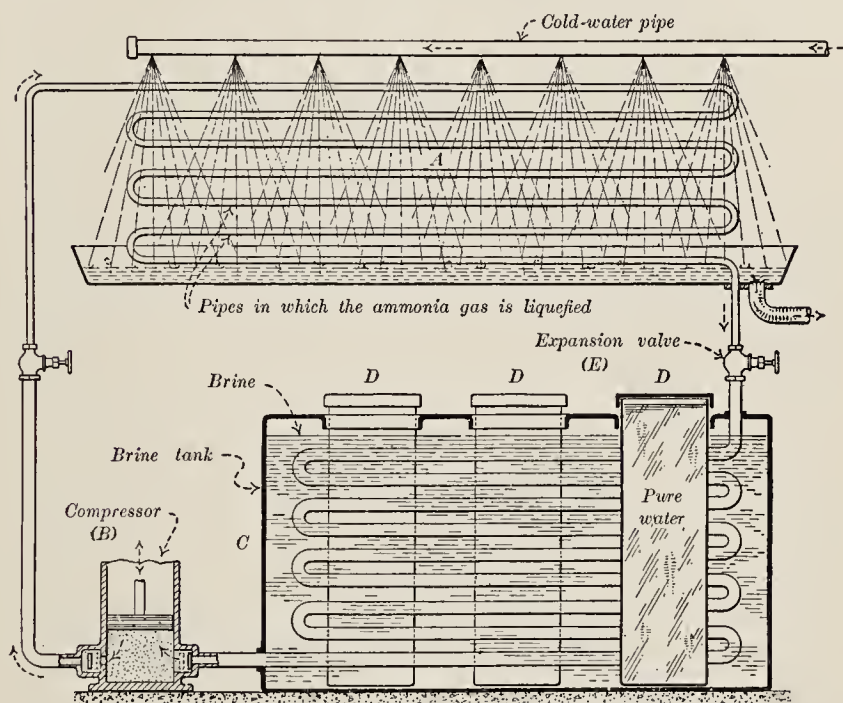


FIG. 53. Drawing illustrating the principle of the ammonia ice machine

ice. The gaseous ammonia is led back to the compressor pump and again liquefied. In a similar way the temperature is kept low in the cold-storage plants now so largely used for preserving food products from decay. The rooms of the plant are supplied with pipes, into which liquid ammonia is forced and allowed to vaporize.

**Crystals.** Crystals may be obtained by cooling melted solids, by the evaporation of solutions, or by cooling the vapors of solids. They are solids bounded by plane surfaces, and these surfaces are arranged in orderly fashion with reference to

coördinate lines drawn through the crystal and called the *crystal axes*. Every crystal has therefore a perfectly definite form. Although there are thousands of these forms, they may all be considered as modifications of six fundamental forms, referred to six arrangements of axes. A general discussion of these forms will be found in the Appendix.

**Crystal structure.** In recent years a great deal has been learned about the structure of crystals. By means of X-ray photography it has been found possible actually to photograph

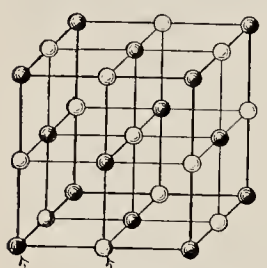


FIG. 54. Drawing illustrating the arrangement of the atoms in a crystal of potassium chloride

the position of the various atoms in a crystal, and to show that they are spaced apart in regular fashion at the intersections of lines drawn through the crystal in the three directions corresponding to the axes. For example, in crystals of the compound potassium chloride, which has the formula  $KCl$ , and which, as we have seen, is formed in the decomposition of potassium chlorate by heat, the atoms of potassium and of chlorine are spaced as shown in Fig. 54. The light spots represent atoms of potassium, and the dark ones atoms of chlorine. It is because of this regular spacing that the crystals assume such definite geometric forms.

**Allotropic forms.** Quite a number of the elements and compounds are known to exist in two or more forms that are related to each other in such a way that one can be converted into the other by the absorption or liberation of energy. Such modifications are called *allotropic forms*. Graphite and the diamond, described on pages 132–135, are two solid allotropic forms of the element carbon.

The change of an element into an allotropic modification is very similar to the change of a solid into a liquid or of a liquid into a gas. The heat absorbed corresponds to the heat of fusion or of vaporization, and the form that has the greater

energy is the most active chemically, just as steam is more active than water, and water than ice.

One of the most interesting instances of an element existing in two allotropic forms, and the one earliest known, is that of *oxygen and ozone*.

**Ozone.** As early as 1785 the Dutch chemist Van Marum noticed the peculiar odor that is often observed near an electrical machine when it is discharging sparks through the air. As the result of a great deal of investigation it has been shown that this odor is due to a definite substance called *ozone*. Under ordinary conditions ozone is a pale-blue gas 1.5 times as heavy as oxygen, and when liquefied it is deep-blue in color and boils at  $-112^{\circ}$ . It can be made from pure oxygen by the action of electrical discharge, and consequently contains no element other than oxygen.

**Preparation of ozone.** Ozone is most easily prepared by passing a silent electric discharge (or electric waves) through oxygen. This is done in an apparatus represented in Fig. 55.

Oxygen enters at *A* and follows the course indicated by the arrows. The metal surfaces *B* and *C* are separated from each other by a space through which the oxygen passes, and are further insulated by the glass *D*. Wires from an induction coil are connected with *B* and *C*. As the oxygen passes upward between the metal plates it is subjected to the electric discharge, and a portion of the oxygen is changed into ozone.

Ozone is also formed in many cases of slow combustion, as when a stick of phosphorus, partly covered with water to keep it from taking fire, is exposed to air (Fig. 56). It is

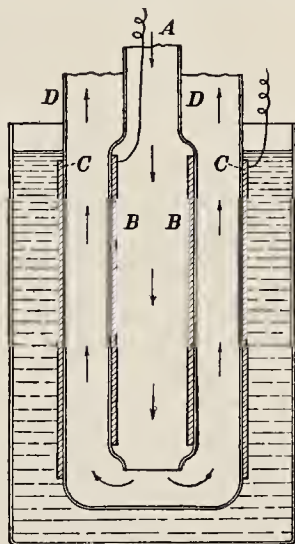


FIG. 55. A convenient form of an apparatus for changing oxygen into ozone



doubtless formed during lightning discharges, but it is doubtful whether any of it is normally present in air, for it is very easily decomposed into ordinary oxygen.

**Conduct and uses of ozone.** Ozone resembles oxygen in many respects, but it is very much more active. Consequently

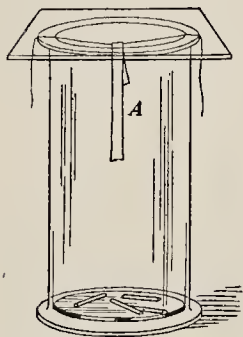


FIG. 56. Drawing showing method of preparing ozone by oxidation of phosphorus

it is a powerful oxidizing agent. It acts upon many colored substances (dyes), converting them into colorless compounds, and on this account is used to bleach certain substances, such as waxes and oils. It destroys some low forms of life and is used as a disinfectant and for purifying water for drinking supplies.

**The energy of ozone.** Ozone is made from oxygen under conditions that add energy to the oxygen. This energy is stored up in the ozone as chemical energy and is available when ozone acts upon other substances. We have seen (p. 103) that the molecule of ozone consists of three oxygen atoms, while that of oxygen consists of but two. Ozone therefore differs from oxygen (1) in chemical energy and (2) in molecular structure. The conversion of oxygen into ozone may be represented in the equation



### EXERCISES

1. What are the conditions which determine the physical state of any element? Illustrate in the case of oxygen.
2. Can all solid substances be melted without decomposition? Illustrate by an example.
3. Can all liquids be boiled without decomposition? Illustrate by an example.
4. When a pond begins to freeze in winter, why does not all the water freeze?
5. Why does a block of ice melt so slowly even in warm air?



6. What becomes of the heat applied to a boiling liquid?
7. Why is it necessary to boil eggs longer on a mountain top than at the seashore in order to cook them?
8. Name three crystalline substances.
9. How can you crystallize common salt?
10. Tubs of water are sometimes placed in cellars in order to prevent the freezing of the stored fruits and vegetables. Is this practice based on scientific grounds?
11. Suppose ice and water to be mixed together at  $0^{\circ}$ . Under what conditions will more water freeze? more ice melt?
12. Suggest a method of raising the boiling point of water above  $100^{\circ}$ .
13. When water freezes in a bottle, why is the bottle broken? Would all other liquids act in the same way?
14. How many calories of heat are given off in the freezing of 500 g. of water at  $0^{\circ}$ ?
15. How many calories are required to change 1 kg. of ice at  $0^{\circ}$  to water at  $70^{\circ}$ ?
16. How many calories are required to change 1 kg. of water at the temperature of your room into steam at  $100^{\circ}$ ?
17. What weight of ice could be melted, by the heat evolved in the condensation of 25 kg. of steam at  $100^{\circ}$ , to water at the same temperature?
18. 50 kg. of ice at  $0^{\circ}$  was placed in a refrigerator. The water resulting from the melted ice absorbed sufficient heat to raise its temperature to  $8^{\circ}$  before it flowed from the refrigerator. Calculate the total number of calories of heat absorbed by the ice and the resulting water.

## CHAPTER XI

### CARBON AND CARBON DIOXIDE

**Introduction.** Everyone is more or less familiar with carbon, for in the impure form of coal it serves as our most common fuel. Charcoal and coke, as well as the black, solid deposit which collects in stovepipes and chimneys and on the bottom of cooking vessels, all consist to a large extent of the free element. In another form carbon assumes entirely different properties, for the diamond is nearly pure carbon. One would not imagine that the black soot which is the dismay of the housewife and the brilliant, highly prized diamond consist wholly of the same element; and yet this is the case, for when burned in oxygen both form one and the same product; namely, the gas known as carbon dioxide. Because of the importance of the element it is desirable that we should learn something of its properties and chemical conduct, and of its most important oxide, namely, carbon dioxide, early in our study.

**Occurrence.** In the uncombined state carbon is found in nature in several forms. The *diamond* is almost entirely pure carbon, while *graphite* and the various forms of *coal* all contain more or less free carbon. The element also occurs abundantly in the form of compounds. Carbon dioxide, which we exhale from our lungs, is its most familiar gaseous compound. Natural gas and petroleum are largely compounds of carbon and hydrogen. Carbon is a constituent of limestone, as well as of many other rocks. All living organisms, both plant and animal (p. 22), contain a large percentage of this element, and the number of its compounds which go to make up the vast variety of animate nature is almost limitless. In the free state carbon occurs in both the crystalline and the amorphous form.

**Crystalline carbon.** Crystalline carbon occurs in two different forms; namely, diamond and graphite.

1. **Diamond.** Diamonds are found in certain localities in South Africa, the East Indies, and Brazil. The crystals as found are usually covered with a rough coating. These are cut so as to bring out the brilliancy of the gem.

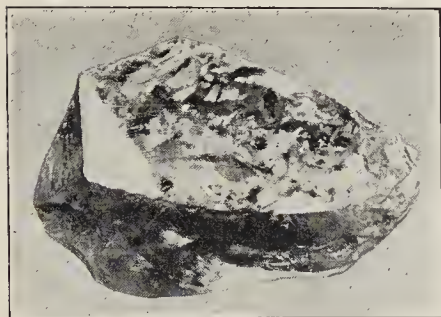


FIG. 57. The Cullinan diamond in its original condition (one half exact size)

The density of the diamond is 3.5, and, though brittle, it is one of the hardest of substances. Few chemical reagents have any action on it, but when heated in oxygen or the air it blackens and burns, forming carbon dioxide.

**Famous diamonds.** The weight of the diamond is usually expressed in carats, a carat being equal to about 0.2 g. The word *carat* is derived from a Greek word meaning "the seed, or bean, of the carob, or locust, tree." The beans were formerly used in weighing diamonds.

The largest diamond known was found in the Transvaal mines in 1905, and weighed  $3025\frac{3}{4}$  carats. This was called the Cullinan diamond (Fig. 57) and was presented to King Edward VII by the Transvaal government. It was subsequently cut into nine large stones and a number of smaller ones. The two largest of these weigh 516.5 and  $309\frac{3}{16}$  carats and are the largest cut diamonds in existence. Other famous diamonds are the Kohinoor ( $106\frac{1}{4}$  carats) (Fig. 58), the Nizam (277 carats), the Victoria (180 carats), and the Jubilee (239 carats).

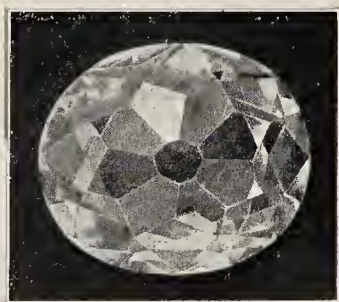


FIG. 58. The Kohinoor diamond (exact size)

**Artificial production of diamonds.** Many attempts have been made to produce diamonds artificially. For a long time these ended in failure, graphite and not diamonds being the product obtained; but

in 1893 the French chemist Moissan (Fig. 120), in his study of chemistry at high temperatures, finally succeeded in making some small ones. He accomplished this by dissolving carbon in melted iron and plunging the crucible containing the solution into water. Under these conditions the carbon crystallized in the iron in the form of the diamond. The diamonds were then freed from the metal by dissolving away the iron in hydrochloric acid.

2. **Graphite.** This form of carbon is found in large quantities, especially in Ceylon, Siberia, and some parts of the

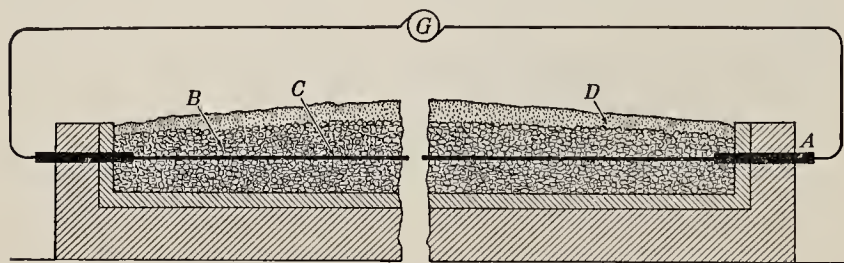


FIG. 59. Electric furnace for the production of graphite

United States and Canada. Large quantities are also made commercially by heating hard coal to a high temperature. It is a glistening black substance, very soft, and greasy to the touch. Its density is about 2.25. It is used in the manufacture of lead pencils and crucibles, as a lubricant, and, in the form of a polish or a paint, as a protective covering for iron (stove polish).

**Commercial production of graphite.** The process devised by the American chemist Acheson (Fig. 132) and carried out on a large scale at Niagara Falls consists in heating hard coal in large electric furnaces about 40 ft. in length, a longitudinal section of one of which is shown in Fig. 59. The electrodes *A* are made of graphite. The furnace is nearly filled with the coarse grains of coal *B*. Since the coal is a poor conductor, there is placed in the center of the charge a core *C* of carbon, which serves to conduct the current through the charge. The charge is covered with a mixture *D* of sand and carbon (or similar materials), which excludes the air. An alternating current is supplied by the generator *G*. Under the



influence of the intense heat produced by the current the carbon is changed into graphite. Prepared in this way, the product is uniform in composition and free from grit, and is therefore generally superior to the natural product.

**Amorphous carbon.** Pure amorphous carbon is best prepared by heating sugar ( $C_{12}H_{22}O_{11}$ ) in the absence of air. The hydrogen and oxygen present are expelled, largely in the form of water, and pure carbon remains. Among the numerous substances that contain amorphous carbon, the following may be mentioned:

1. **Coal and coke.** The various forms of coal were formed from vast accumulations of vegetable matter. In hard coal (anthracite) nearly all the carbon is in the uncombined state, while in soft, or bituminous, coal a considerable portion of the carbon is combined with hydrogen, oxygen, nitrogen, and sulfur. When soft coal is heated in the absence of air, complex changes occur, resulting in the formation of various useful compounds of carbon, which are given off in the form of gases and vapors, while the mineral matter and free carbon remain and constitute ordinary *coke*. The matter which escapes when coal is heated in the absence of air is known as *volatile matter*. In hard coal the volatile matter averages from 5 per cent to 8 per cent, while in soft coal it averages from 30 per cent to 35 per cent. When coal is burned, the mineral matter present is left in the form of *ash*.

2. **Charcoal.** This is prepared from wood just as coke is prepared from coal. The volatile matter formed in the process and expelled consists of many valuable substances, such as *wood alcohol* and *acetic acid*, which are obtained commercially in this way. Formerly much of this volatile matter was allowed to escape, but at present an increasing amount of charcoal is prepared in such a way that the volatile matter is condensed and saved and serves many useful purposes. Both charcoal and coke are used as fuels, and they are especially useful in reducing metals from their oxides, as will be described later.



**Modern methods for the production of charcoal.** Iron cars are loaded with wood, *A, A* (Fig. 60), and run into the retort *B*. The retort is then made air-tight and heated slowly for twenty-four hours by the fires *F, F*. The gaseous products escape through the pipes *C, C* and then pass into the condensers *D, D*. Here those portions which are liquid at ordinary temperatures, such as wood alcohol and acetic acid, are condensed, while the gaseous products are led back into

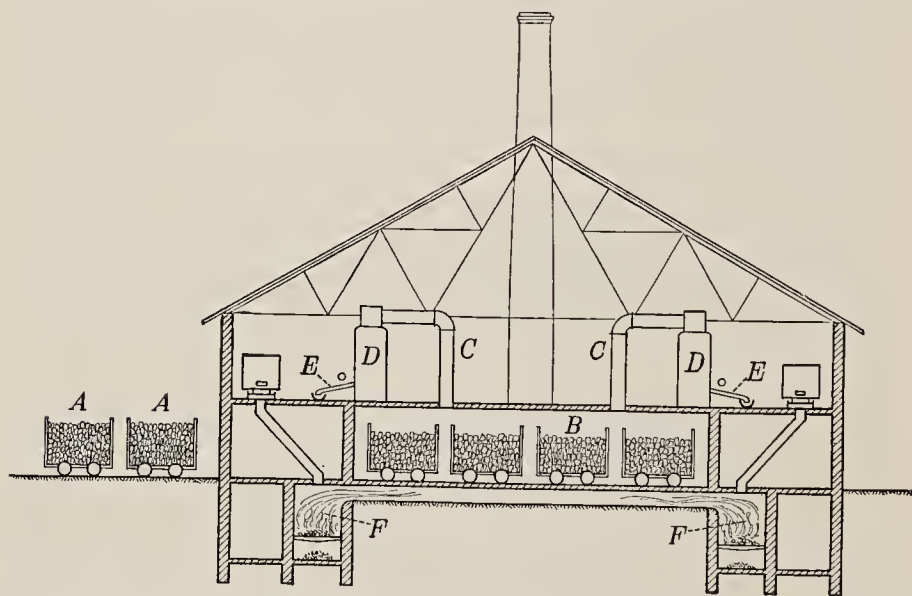


Fig. 60. Drawing illustrating the modern method for the production of charcoal

the furnace and burned. When all the volatile matter has been expelled in this way, the cars containing the charcoal are run into cooling chambers, and their place in the retort is taken by other cars loaded with wood.

3. **Boneblack, or animal charcoal.** This is made by charring bones and animal refuse. It consists of calcium phosphate and very finely divided carbon, and is especially useful for removing coloring matter in the refining of sugar.

4. **Carbonblack; lampblack.** The black powders known as carbonblack and lampblack are products of the imperfect combustion of carbonaceous fuels, such as oil and gas.

**Destructive distillation.** The process of decomposing such substances as coal, wood, and bones by heating them in the absence of air is termed *destructive distillation*. Thus, we say that coke, charcoal, and boneblack are made by the destructive distillation of coal, wood, and bones, respectively.

**Properties of carbon.** While the various forms of carbon differ in many properties, especially in color and hardness, yet they are all odorless, tasteless solids, insoluble in water. Only in the intense heat of the electric arc does carbon volatilize, passing directly from the solid state into a vapor without melting.

In the form of boneblack, carbon withdraws certain kinds of organic matter from solutions; hence its use in refining sugar and other substances. A marked property of carbon is its ability to take up (or, in chemical terms, to *adsorb*) large volumes of gases. The amount of gas adsorbed by any given sample of carbon depends not only on the material from which the carbon is prepared but also on the method of preparation.



FIG. 61. A form of gas mask used in the World War as a protection against poison gas

**Gas masks.** The use of various poison gases in the World War made it necessary to devise gas masks for the protection of the troops. Many different kinds of masks were used, but as finally developed these were made and fitted to the face (Fig. 61) in such a way that all the inhaled air had to pass through a light metal box (canister) filled with layers of various materials, the chief of

which was charcoal. These materials either adsorbed or combined with the poison gases. They were so efficient that *phosgene*, one of the most dangerous of these gases, when present in the ratio of 1000 parts of gas to 1,000,000 parts of air, could be reduced to one part per million in the small fraction of a second required for the air to pass through the canister.

**Activated charcoal.** All charcoal possesses the power of adsorbing gases to a greater or less extent, depending primarily upon the amount of surface exposed in unit volume of charcoal. During the World War great effort was made to prepare for use in gas masks a charcoal which should have this property to a high degree. It was found that this could be done by using a very definite heat treatment in the preparation of the charcoal, and then *activating* the product by heating it in the presence of a little air or, in some cases, of steam. Such charcoal is known as *activated charcoal*. It is very porous and adsorbs large volumes of gases. The best charcoal for this purpose is made from some very dense material like coconut shells and peach stones.

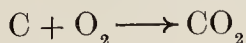
**Chemical conduct.** At ordinary temperatures carbon is a very inert substance, but at higher temperatures it combines directly with most of the elements. Because of its strong affinity for oxygen *it is an excellent reducing agent*. Its compounds with the metals are called *carbides*. One of the most important of these is *calcium carbide* ( $\text{CaC}_2$ ), which is used in the preparation of acetylene. When carbon or a substance containing it, such as wood or coal, burns, the element combines with oxygen to form *carbon dioxide* ( $\text{CO}_2$ ); if the oxygen supply is limited, some carbon monoxide ( $\text{CO}$ ) will be formed also. Both of these oxides are colorless gases.

**Uses of carbon.** The chief use of amorphous carbon is for fuel to furnish heat and power for all the uses of civilization. An enormous quantity of carbon in the form of coal, coke, and charcoal is used as a reducing agent in the separation of the various metals from their ores. Carbonblack is used for making motor-car tires, indelible ink, printer's ink, paints, and black varnishes, while boneblack and charcoal are used in

filters. In the refining of sugar the dark solution of the impure compound is filtered through charcoal or boneblack, which removes the coloring matter. On evaporation the resulting solution yields the colorless sugar. Activated charcoal is used in refining various products and in making gas masks for protecting workmen in certain industries from the evil effects of poisonous gases evolved in industrial operations.

**Carbon dioxide ( $\text{CO}_2$ ) (carbonic acid gas).** Carbon unites with oxygen to form three different compounds. The most common of these is the colorless, odorless gas known as *carbon dioxide* or *carbonic acid gas*. It is important for us to study the properties of this compound at present. The discussion of the other oxides will be deferred to a later chapter.

A person may have known little about carbon dioxide, yet it is a compound with which he has always been closely associated, for it is present in the air, although in small percentages. It is formed in the process of respiration. The air exhaled from the lungs contains as much as 4 or 5 per cent of the gas. It is also formed whenever carbon or any compound of carbon burns in oxygen or in the air.



Since all the common fuels, such as coal, wood, oil, and gas, contain carbon, either in a free or in a combined state, it follows that carbon dioxide is formed whenever these fuels are burned. It is likewise formed in the making of lime by heating limestone, as well as in the process of fermentation which takes place in the manufacture of alcohol and alcoholic liquors. Large quantities of it escape from volcanoes and from crevices in the earth. It is present in the air to the extent of about 3 parts in 10,000, and this apparently small percentage is of fundamental importance in nature, as will be pointed out in the discussion of the atmosphere.

**Properties.** Carbon dioxide is one of the heaviest of gases, 1 liter weighing 1.9768 g. Its weight may be inferred from the fact that it can be poured like water from one vessel



downward into another; or, as a more striking experiment, the gas may be poured from a cylinder *A* into a beaker *B* attached to a balance and counterpoised as shown in Fig. 62. At  $15^{\circ}$  and under ordinary pressure 1 volume of water dissolves 1 volume of the gas. It is rather easily condensed to a colorless solid, which, under atmospheric pressure, evaporates without melting at  $-78.5^{\circ}$ .

Carbon dioxide is not regarded as a poisonous gas, although one could not live more than a few hours in an atmosphere

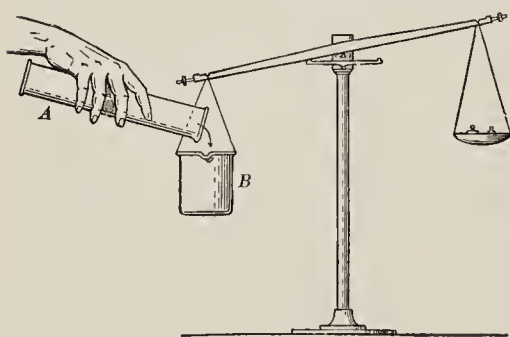


FIG. 62. Illustrating the method for showing that carbon dioxide is heavier than air

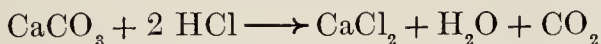
containing as much as 25 per cent of the gas. In an atmosphere of the pure gas, death would quickly follow because of lack of oxygen.

**Liquid and solid carbon dioxide.** The commercial carbon dioxide compressed in steel cylinders is under such great pressure that it is largely in the liquid

state. When the pressure is removed, the rapid vaporization of the liquid reduces the temperature sufficiently to freeze a portion of the escaping liquid to a snowlike solid. Cylinders of liquid carbon dioxide are inexpensive and should be available in every school.

To prepare the solid carbon dioxide the cylinder should be placed across the table and supported in such a way that the stopcock end is several inches lower than the other end. A loose bag is made by holding the corners of a piece of cloth around the neck of the stopcock. The stopcock is then turned on so that the liquid rushes out in large quantities. A considerable quantity of the snow very quickly collects in the cloth. If some of this solid is placed in an evaporating dish and covered with ether (the liquid so largely used as an anæsthetic in surgical operations), the temperature of this mixture falls below  $-100^{\circ}$ . If a few drops of mercury (the liquid used in thermometers) are added to the mixture, the mercury quickly freezes to a solid resembling lead.

**Preparation.** In the laboratory, carbon dioxide is prepared by the action of hydrochloric acid on the compound known as calcium carbonate ( $\text{CaCO}_3$ ). The latter is found in nature in many different substances, such as shells, coral, and limestone. Marble is nearly pure calcium carbonate, and, being comparatively inexpensive, is the material most often used in the preparation of carbon dioxide. When hydrochloric acid and marble are brought in contact with each other, water, calcium chloride ( $\text{CaCl}_2$ ), and carbon dioxide are formed according to the following equation:



The calcium chloride is a soluble white solid which remains in solution, while the carbon dioxide escapes and is collected by the displacement of air as described below.

**Laboratory apparatus.** The gas may be prepared in the apparatus shown in Fig. 63. Pieces of marble are placed in flask *A*, and hydrochloric acid diluted with an equal volume of water is slowly added through the funnel tube *B*. The tube *C*, through which the carbon dioxide escapes as fast as formed, passes through a piece of cardboard placed over the mouth of a bottle or cylinder, as shown in the figure. The gas is heavier than air and gradually fills the cylinder, pushing out the air. A lighted splint brought into the mouth of the cylinder is extinguished when the cylinder is filled with the gas.

The Kipp apparatus (Fig. 16) is more convenient than the simple apparatus shown in Fig. 63. It is used as in the preparation of hydrogen, marble being substituted for the zinc.

**Commercial preparation.** On a large scale carbon dioxide is obtained by the combustion of coal. The compound is separated

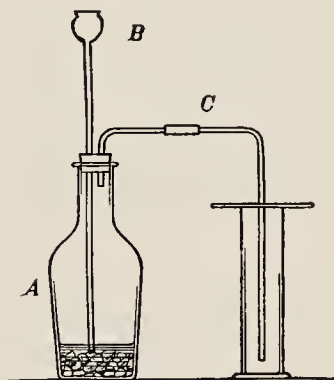


FIG. 63. A simple apparatus for preparing carbon dioxide by the action of hydrochloric acid on marble

from the other gases also formed when the coal burns, and is stored by pumping it into iron cylinders similar to those used in storing oxygen (Fig. 6). In this form it is a common article of commerce.

**Chemical conduct.** Carbon dioxide is a very stable compound. It is neither combustible nor a supporter of combustion.

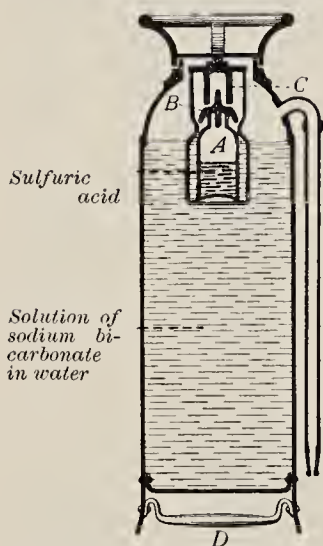
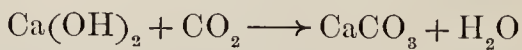


FIG. 64. A modern fire extinguisher in which water and carbon dioxide are used to extinguish the flame

A simple test for detecting the presence of the gas is based upon the reaction of the gas with limewater. The limewater is a clear solution of calcium hydroxide, a white solid compound having the formula  $\text{Ca(OH)}_2$ , usually written  $\text{Ca(OH)}_2$ . When carbon dioxide is bubbled through this solution, calcium carbonate ( $\text{CaCO}_3$ ) forms as follows:



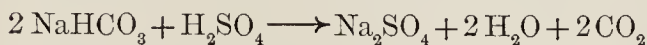
The calcium carbonate is a white solid and, being insoluble, separates from solution as fast as it is formed, producing a cloudy or milky appearance.

**Uses.** The carbon dioxide in the air is a food for plants, as will be shown in the chapter on the atmosphere.

Commercially it is used chiefly in the manufacture of soda water and similar beverages and as a fire extinguisher. Ordinary soda water consists of various flavoring extracts to which is added water charged with carbon dioxide under pressure. When the pressure is removed, the excess of gas escapes, producing *effervescence*. A burning candle is extinguished in air which contains as little as 2.5 per cent of carbon dioxide; hence the dioxide is used as a fire extinguisher.

**Portable fire extinguishers.** Familiar types of portable fire extinguishers are shown in Figs. 64, 65. That shown in Fig. 64 is

a device for generating carbon dioxide under pressure. The liquid is a solution of sodium bicarbonate (ordinary baking soda ( $\text{NaHCO}_3$ )) in water contained in a metal cylinder. The bottle *A* contains sulfuric acid. In case of fire the apparatus is grasped by the handle *D*, and the apparatus is inverted. The stopper *B* drops onto the support *C*, thus allowing the acid in the bottle *A* to flow out into the solution of sodium bicarbonate. The acid at once reacts with the sodium bicarbonate, generating carbon dioxide, thus:



Some of the gas dissolves in the water, while the rest forces the water out through the nozzle *E*. While the volume of water so obtained is not large, it is very effective as a fire extinguisher because of the carbon dioxide accompanying it. The type of extinguisher shown in Fig. 65 is a smaller metal cylinder filled with the liquid known as carbon tetrachloride ( $\text{CCl}_4$ ) and fitted with a sort of piston for forcing the liquid out in case of fire. The liquid is not combustible and is quite volatile; hence when it is thrown onto a fire it volatilizes and, the vapor being heavy, surrounds the burning body and prevents the oxygen of the air from coming in contact with it.

**Quantitative determination of carbon and hydrogen.** Fig. 66 illustrates the method used by a chemist in determining the amount of carbon and hydrogen (say) in a sample of coal. A small amount of the sample is weighed out in a narrow porcelain dish *A* and slipped into the glass tube *B*. The remaining part of the tube is filled with an oxidizing agent, usually copper oxide. The glass tube *B* is gradually heated to a red heat, while a slow current of air, dry and free from carbon dioxide, is passed continuously into the tube at *C*. Under these conditions the carbon and the hydrogen in the coal burn to carbon dioxide and water respectively; these products of combustion then pass through the narrow tube *D* into the tube *E* filled with pieces of solid calcium chloride, which absorbs the water present. The carbon dioxide passes



Fig. 65. A modern fire extinguisher in which carbon tetrachloride is sprayed upon the flame



on into *F*, which contains a solution of potassium (or sodium) hydroxide and is absorbed. The tubes (including contents) *E* and *F* are weighed before and after the coal is burned; the increase

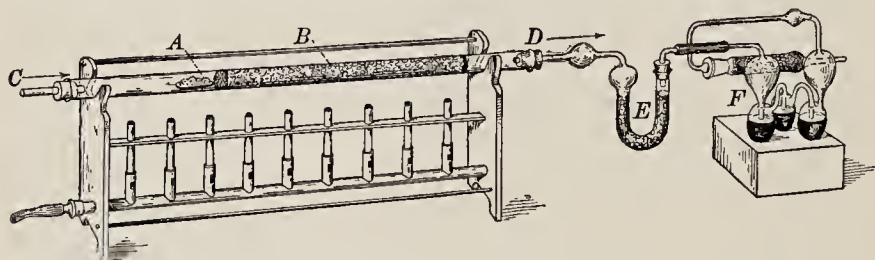


FIG. 66. Apparatus for determining the percentage of carbon and hydrogen in coal

in weights gives respectively the weights of the water and carbon dioxide formed, and from these weights the percentage of hydrogen and carbon present can be calculated.

### EXERCISES

1. Suggest a method for proving that all the various forms of carbon described are really carbon.
2. How could you judge of the relative purity of different forms of carbon?
3. How could one easily distinguish between oxygen, hydrogen, and carbon dioxide?
4. Apart from its color, why should carbon be useful in the preparation of inks and paints?
5. Why does soda water effervesce?
6. How could you prove that carbon dioxide is a product of combustion?
7. Suppose the Kohinoor diamond were to be burned in oxygen, calculate the volume of the product of combustion.
8. (a) Calculate the weight of 100 liters of carbon dioxide. (b) What weight of marble is necessary for the preparation of this volume of the gas? (c) What weight of calcium chloride would be formed in this process?
9. What weight of calcium carbonate would be necessary to prepare sufficient carbon dioxide to saturate 10 liters of water at 15° and under ordinary pressure?

10. The average person exhales about 8 liters of air per minute, containing about 4 per cent of carbon dioxide by volume. Calculate the number of liters of carbon dioxide exhaled by such a person in twenty-four hours.

11. It is estimated that over a billion tons of coal is consumed annually. (a) Upon the supposition that the coal consumed averages 80 per cent carbon, what weight of carbon dioxide would be added to the atmosphere in the combustion of a billion tons?

12. Calculate the percentage of carbon and hydrogen present in a fuel from the following data: 1.5236 of the fuel was burned as in Fig. 66. The increase in the weight of tube *E* amounted to 0.4012 g., while that of tube *F* was 3.9182 g.

13. A portable fire extinguisher (Fig. 64) contained 5 kg. of sodium bicarbonate. (a) What weight of sulfuric acid would be required to react with this amount of carbonate? (b) What volume of carbon dioxide would be generated, measured at 18° and 752 mm.?

14. The air of a room was tested for carbon dioxide by drawing 100 liters of it through weighed bulbs containing a solution of potassium hydroxide (Fig. 66, *F*). The temperature was 15° and the pressure 750 mm. The increase in the weight of the bulbs was 0.08 g. What was the percentage by volume of carbon dioxide in the air of the room?

## CHAPTER XII

### VALENCE; DIFFERENT KINDS OF FORMULAS

**Definition of valence.** Among the various compounds which we have met so far in our study are two, namely, hydrogen chloride ( $\text{HCl}$ ) and water ( $\text{H}_2\text{O}$ ), each of which consists of hydrogen joined to one other element. A little later we shall meet with a number of other compounds of this same general character. For example, we shall study the gaseous compound known as ammonia ( $\text{NH}_3$ ), whose aqueous solution constitutes the well-known *aqua ammonia* of the druggist; also the compound known as methane or marsh gas ( $\text{CH}_4$ ), which is the chief constituent of natural gas and coal gas. In order that we may compare the formulas of these compounds of hydrogen we will place them as follows:

$\text{HCl}$   
(hydrogen chloride)

$\text{H}_2\text{O}$   
(water)

$\text{H}_3\text{N}$   
(ammonia)

$\text{H}_4\text{C}$   
(marsh gas)

An inspection of the above formulas shows that each of these compounds is made up of hydrogen combined with one other element; also that *the atoms of the various elements differ among themselves in the number of hydrogen atoms with which they combine*. Thus, an atom of chlorine combines with but one atom of hydrogen, while an atom of oxygen combines with two, one of nitrogen with three, and one of carbon with four.

These observations bring into view an important property of the atoms, called *valence*. *The valence of an atom is that property which determines how many atoms of any other kind it can hold in combination or can displace in a reaction.*

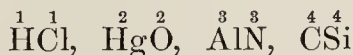
**Standard of valence.** Since, as a rule, neither an atom of hydrogen nor an atom of chlorine combines with more than

one atom of any other element (to form a compound which contains only two kinds of atoms) they are called *univalent* atoms and serve as a standard for the valence of other atoms. Oxygen, sulfur, iron, and zinc, whose atoms combine with two of hydrogen or of chlorine, are called *bivalent*. There are other elements whose atoms have still higher valences, of three (trivalent), of four (quadrivalent), and so on up to a valence of eight.

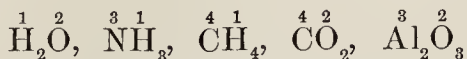
From all that has been said it might be inferred that in the compound CuO the atoms both of copper and of oxygen are univalent, because there is one of each in the molecule of copper oxide. But, *measured by hydrogen*, oxygen is bivalent ( $\text{H}_2\text{O}$ ). As we shall see below, copper must be bivalent also. We must always keep in mind that oxygen is bivalent when we deduce the valence of an element from the formula of its oxide.

**Applications of valence.** While it is not possible at this point to go very far into the subject of valence, the following principles, which generally hold, will be of service:

1. If two elements which have the same valence combine to form a compound, they will combine atom for atom, as shown in the following formulas, in which the valence of the atom of each element is designated by the figure above the symbol:



2. If two elements which have different valences combine to form a compound, then such numbers of atoms of the two elements will combine as will add up an equal number of valences, thus:

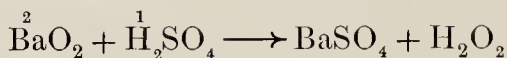
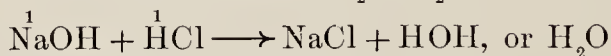
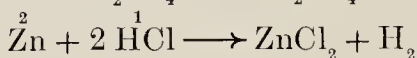
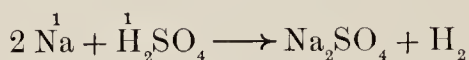


Hydrogen is univalent, while oxygen is bivalent, as is expressed by the figures over the formula of water. There is 1 atom of oxygen (2 valences); hence there must be a sufficient number of hydrogen atoms to add up 2 valences; namely, 2 atoms.

Again, in the formula  $\text{CO}_2$  the carbon is quadrivalent. Hence, for each atom of carbon (4 valences) there must be 2 atoms of oxygen (4 valences). ~



3. In any reaction in which one element takes the place of another in a compound, or one in which one element of a compound exchanges places with an element in another compound, the exchange must be between such numbers of atoms of the two elements involved as will add up an equal number of valences; for example, one atom of a bivalent element will displace two atoms of a univalent element, while two atoms of a trivalent element (6 valences) will displace three atoms of a bivalent element (6 valences). The following equations will suffice to illustrate this principle:



**Variable valence.** It often happens that two given elements form more than one compound, and in such cases at least one of the elements must have more than one valence. We consider oxygen to be almost always bivalent, so that in the oxide CO carbon must be bivalent, while in the oxide CO<sub>2</sub> it is quadrivalent. Similarly, mercury forms two chlorides, HgCl and HgCl<sub>2</sub>, in which the mercury is univalent and bivalent respectively. In general it is true that each element has one valence that is much more frequently exerted than any other, so that we can think of a given element as having in the main a certain valence and less frequently some other valence.

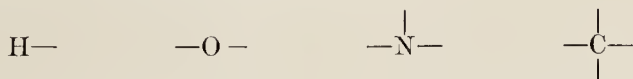
**Difficulties.** While the general idea of valence is of great assistance, yet it must be added that the student will meet with many cases which, at first sight at least, are misleading. Thus, in the formula for hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, one would be inclined to say that hydrogen and oxygen have the same valence; while the formula for iron oxide, Fe<sub>3</sub>O<sub>4</sub>, would indicate that if the oxygen is bivalent, then the iron has a valence

of  $2\frac{2}{3}$ , which is an absurdity. These cases, however, are not numerous and will be explained in later chapters. The usual valences of the elements will become familiar as we study the formulas of their compounds. In the following table are given the usual valences of a few of the most important elements.

## VALENCE OF ELEMENTS

Univalent . . . . .	H, Na, K, Ag, Cl, Br, I
Bivalent . . . . .	Ca, Ba, Mg, Zn, Hg, Fe, S, O
Tervalent . . . . .	Al, Bi, As, Sb, Fe, N, P
Quadrivalent . . . . .	Sn, C, Si, S
Quinivalent . . . . .	N, P, As, Sb

**Method of representing valence.** It is often convenient to represent the valences of elements in a graphic way, and this is commonly done by lines drawn from the symbols of the elements, one line (or *bond*, as it is often called) expressing a single valence. In this way we may represent the valence of hydrogen (univalent), oxygen (bivalent), nitrogen (tervalent), and carbon (quadrivalent) as follows:



When hydrogen unites with oxygen to form water ( $\text{H}_2\text{O}$ ), we have every reason for believing that each of the two atoms of hydrogen is combined directly with oxygen, and this fact can be expressed by the formula  $\text{H}-\text{O}-\text{H}$  or, more simply,  $\text{H}-\text{O}-\text{H}$ , in which the two valences of the hydrogen atoms *saturate* the two valences of the oxygen atom. Such a formula is known as a *structural formula*.

**Different kinds of formulas.** As we proceed with our study of chemistry we shall meet with two different kinds of formulas.

1. **Empirical formulas.** The ordinary type of formula used, such as  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CO}_2$ , simply expresses the composition of the molecules of the compounds, giving the elements present in the molecules and the number of atoms of each. Such formulas are called *empirical formulas*.

2. *Structural formulas*, on the other hand, not only represent the composition of the molecules, but in addition attempt to give us some idea of the arrangement of the atoms within the molecule. Thus, the formula  $\text{H}-\text{O}-\text{H}$  (see preceding paragraph) tells us not only that the molecule of water contains two atoms of hydrogen and one of oxygen, but also that each of the hydrogen atoms is combined directly with the oxygen atom. Evidently there would be no difference between the formulas  $\text{H}-\text{O}-\text{H}$  and  $\overset{\text{H}}{\text{H}} > \text{O}$ , for each would express the same facts; namely, that the molecule of water is composed of two atoms of hydrogen and one of oxygen, and that each of the hydrogen atoms is joined directly to the oxygen atom.

Structural formulas do not imply that the atoms in the molecule are held rigidly; in fact, we are certain that the atoms are in motion. But this motion does not change the relation of one atom to another, just as the motion of the heavenly bodies that constitute the solar system does not change the relation of one planet to another.

The following examples will serve to illustrate the difference between empirical and structural formulas:

Empirical formula	$\text{HCl}$	$\text{H}_2\text{O}$	$\text{H}_3\text{N}$	$\text{H}_4\text{C}$
Name of compound	hydrogen chloride	water	ammonia	methane
Structural formula	$\text{H}-\text{Cl}$	$\text{H}-\text{O}-\text{H}$	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{N}-\text{H} \end{array}$	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$

**Derivation of structural formulas.** The derivation of the structural formulas of compounds is a very difficult problem, and there are many compounds whose structural formulas are not known, although much experimental work has been done to determine them. The derivation of these formulas is not a matter of simply combining the elements present in the molecule in such a way that each element has its proper valence; the formula must be an expression of the true relation of each atom to the others, and this is not easy to determine.

It is beyond the scope of this book to discuss the methods used in deriving structural formulas; nevertheless it is sometimes convenient to use them, and we shall not hesitate to do so if their use helps to make the subject under discussion more easily understood. The student will have to accept such formulas as an expression of the truth, and look forward to a more advanced course if he wishes to understand just how they are derived.

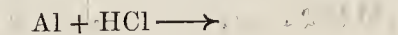
**The cause of valence.** If it be asked, Why do atoms differ in valence, so that one atom of chlorine can combine with but one of hydrogen, while one of oxygen can combine with two? the answer will have to be that we do not know. It seems probable, however, that the cause is to be found in the capacity of atoms of the various elements to take up different charges of electricity. The question will be discussed more in detail in a later chapter.

### EXERCISES

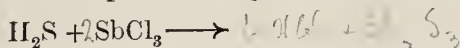
1. Assuming that hydrogen is always univalent and oxygen always bivalent, state the valence of each of the elements in the following compounds:  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{P}_2\text{O}_3$

2. Aluminum and carbon form a compound in which the aluminum is trivalent and the carbon quadrivalent. What is its formula?

3. Aluminum (trivalent) in contact with hydrochloric acid displaces the hydrogen of the acid, liberating free hydrogen. Complete and balance the following equation:

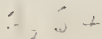


4. Complete and balance the following equation, representing a reaction in which the hydrogen of the compound  $\text{H}_2\text{S}$  (hydrogen sulfide) and the antimony (Sb) of the compound  $\text{SbCl}_3$  replace each other:



5. Sulfur unites with oxygen to form two different compounds in which the sulfur is respectively quadrivalent and hexavalent. Write the formula of each of the oxides.

6. When the gas hydrogen sulfide ( $\text{H}_2\text{S}$ ) is bubbled through a solution of the chloride of copper  $\text{CuCl}_2$ , the hydrogen and the copper exchange places. Write the equation for the reaction.



## CHAPTER XIII

### THE ATMOSPHERE

**Historical.** The terms *atmosphere* and *air* are often used interchangeably, although, strictly speaking, the former term is applied to the entire gaseous envelope surrounding the earth, while the latter is applied to a limited portion of this envelope. We are surrounded by the atmosphere, but we breathe the air. Like water, air was formerly regarded as an element. Near the close of the eighteenth century, however, through the experiments of Scheele, Priestley, Cavendish, and Lavoisier, it was shown to be a mixture of at least two gases, —those which we now call oxygen and nitrogen. By absorbing the oxygen from an inclosed volume of air and measuring the contraction in volume caused by the removal of oxygen, Cavendish was able to determine with considerable accuracy the relative volumes of oxygen and nitrogen.

**Composition of the air.** The normal constituents of air, together with the approximate volumes of each in samples collected in the open fields, are as follows:

Oxygen . . . . .	21 volumes in 100 volumes of dry air
Nitrogen . . . . .	78 volumes in 100 volumes of dry air
Water vapor . . . . .	variable within wide limits
Carbon dioxide . . . . .	3 to 4 volumes in 10,000 volumes of dry air
Argon . . . . .	0.940 volumes in 100 volumes of dry air
Helium, neon, krypton, xenon	traces

In addition, there are usually present small quantities of hydrogen peroxide, oxides of nitrogen, microorganisms, dust particles, and traces of hydrogen. The air in large cities and manufacturing districts is also likely to contain certain gases



evolved in manufacturing processes. Among these are hydrogen sulfide ( $\text{H}_2\text{S}$ ) and sulfur dioxide ( $\text{SO}_2$ ).

**Water vapor in the air.** The quantity of water vapor which may be present in the air varies with the temperature. This is shown in the following table, which gives the weight in grams of the water vapor that 1 cu. m. of air can absorb at the temperature indicated:

Temperature . . . . .	0°	10°	20°	30°
Weight of water . . . . .	4.8 g.	9.9 g.	17.1 g.	30 g.

**The constituents of the air that are essential to life.** The constituents that are known to be essential to life are oxygen, nitrogen, water vapor, and carbon dioxide.

The oxygen in the atmosphere directly supports life through the process of respiration. The nitrogen serves to dilute the oxygen and thus to diminish the intensity of its action. It is likewise assimilated by certain plants (p. 90). The water vapor prevents excessive evaporation of the water present in organisms, while the carbon dioxide is an essential plant food.

**The quantitative analysis of air.** A number of different methods have been devised for the determination of the percentages of the constituents of the atmosphere. Among these are the following:

1. **Determination of oxygen.** The oxygen is withdrawn, by means of phosphorus, from a measured volume of air inclosed in a tube.

**Experimental details.** To make the determination a graduated tube is filled with water and inverted in a vessel of water. A sample of the air to be analyzed is then introduced into the tube until the tube is nearly filled with the gas, and the volume is carefully noted. A small piece of phosphorus is attached to a wire and brought within the tube as shown in Fig. 67. After a few hours the oxygen in the inclosed air will

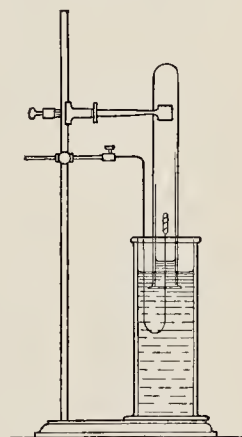


FIG. 67. The determination of the oxygen in air by means of phosphorus

have combined with the phosphorus, the water rising to take its place. The phosphorus is removed, and the volume of the gas again noted. The contraction in the volume is equal to the volume of oxygen absorbed from the air.

2. *Determination of nitrogen.* If the gas left after the removal of oxygen from a portion of air is passed over heated magnesium, the nitrogen present in the gas is withdrawn, leaving argon and the other rare elements. It may thus be shown that, of the 79 volumes of gas left after the removal of the oxygen from 100 volumes of dry air, approximately 78 volumes are nitrogen and 0.94 argon. The other elements are present in such small quantities that they may be neglected.

3. *Determination of water vapor and carbon dioxide.* These constituents are determined by passing a known volume of air through two tubes, the first containing calcium chloride and the second sodium hydroxide or potassium hydroxide (see Fig. 66). The calcium chloride removes the moisture, while the sodium hydroxide removes the carbon dioxide. The tubes (including contents) are weighed before and after the air is passed through them, and the increase in the weights will give the weights of moisture and carbon dioxide respectively in the original volume of air.

**Processes tending to change the composition of the air.** These processes fall into two classes: those which increase the carbon dioxide and those which diminish it.

1. *Processes tending to increase the quantity of carbon dioxide.* Not only do large quantities of carbon dioxide escape into the atmosphere from volcanoes and crevices in the earth's crust, but certain processes are constantly taking place which are attended by evolution of this gas. Chief among these are the following: (a) *Respiration.* In this process some of the oxygen in the inhaled air is absorbed by the blood and carried to all parts of the body, where it combines with the carbon present in the compounds provided by the body as fuel, or with the waste tissues of the body. The reaction is attended by

a transformation of chemical energy into heat and muscular energy. The products of oxidation are carried back to the lungs and exhaled largely in the form of carbon dioxide. (b) *Combustion*. All the ordinary fuels contain large percentages of carbon. When burned, this is oxidized to carbon dioxide. (c) *Decay of organic matter*. When organic matter decays in the air the carbon present is oxidized to carbon dioxide.

2. *Processes tending to decrease the quantity of carbon dioxide*. There are two general processes which tend to diminish the quantity of carbon dioxide in the atmosphere.

(a) *The action of plants*. Plants have the power, when growing in sunlight, of absorbing carbon dioxide from the air; they retain the carbon and return a portion of the oxygen to the air. It is from this source that plants obtain their entire supply of carbon.

**Laboratory experiment.** That plants evolve oxygen in the sunlight may be shown as follows: Some freshly gathered leaves are placed under water in the jar *A* (Fig. 68) and covered with the funnel *B*, the stem of which extends into the graduated tube *C*. Bubbles of oxygen make their escape from the surface of the leaves and may be collected in the measuring tube *C*.

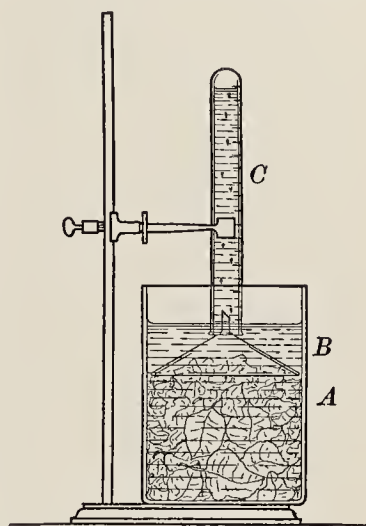


FIG. 68. The liberation of oxygen from plants exposed to sunlight

(b) *The weathering of rocks*. Large quantities of carbon dioxide are being constantly withdrawn from the atmosphere by combination with various rock materials.

**Composition of the air constant.** Notwithstanding the changes taking place which tend to alter the composition of the air, the results of the analyses of air show that the percentages of oxygen and nitrogen, as well as of carbon dioxide, are very

nearly constant. Indeed, so constant are the percentages of oxygen and nitrogen that the question has arisen, Is the air a definite chemical compound?

**Air a mixture.** That the oxygen and nitrogen in the air are not combined may be shown in a number of ways, among which are the following:

1. When air dissolves in water, it has been found that the ratio of oxygen to nitrogen in the dissolved air is no longer 21 : 78, but more nearly 35 : 65. If air were a chemical compound, the ratio of oxygen to nitrogen would not be changed by solution in water.

2. A chemical compound in the form of a liquid has a definite boiling point at a given pressure (p. 120). For example, water boils at  $100^{\circ}$  under standard pressure. Moreover, the steam which is formed has the same composition as the water. The boiling point of liquid air, on the contrary, gradually rises as the liquid boils, the nitrogen escaping first, then the oxygen. If the two were combined, they would pass off together in the ratio in which they are found in the air.

3. Another reason for regarding the air as a mixture is the fact that when oxygen and nitrogen are mixed together, heat is neither evolved nor absorbed in the process.

**Why the air has a constant composition.** If air is a mixture and changes are constantly taking place which tend to modify its composition, how, then, do we account for the constancy of composition which the analyses reveal? This is explained by several facts: (1) The changes which are caused by the processes of combustion, respiration, and decay on the one hand, and the action of plants on the other, tend to equalize each other. (2) The winds keep the air in constant motion and so prevent local changes. (3) The volume of the atmosphere is so vast and the changes which occur are so small, compared with the total volume, that they cannot be readily detected. (4) Finally, it must be noted that only air collected in the open fields shows this constancy in composition. The air in a poorly ventilated room occupied by a number of people rapidly changes in composition.



**Impure air and ventilation.** The difference in the percentages of oxygen, carbon dioxide, and moisture present in inhaled and exhaled air are shown in the following table:

CONSTITUENT	INHALED AIR	EXHALED AIR
Oxygen . . . . .	21.00%	16.00%
Carbon dioxide . . . . .	0.04%	4.38%
Water vapor . . . . .	variable	saturated

The injurious effects resulting from inadequate ventilation seem to be due neither to lack of oxygen nor to the excess of carbon dioxide; rather they are due to high temperature and to the presence of an abnormal amount of water vapor; both of these conditions are apt to prevail in crowded and poorly ventilated rooms.

Not only is water vapor exhaled from the lungs, but there is constant evaporation of moisture from the pores of the skin, and in this process much heat is absorbed. Notwithstanding the extreme changes in the temperature of the air, the temperature of the body in health remains nearly constant. It is partly by variations in the amount of moisture evaporating from the skin that the temperature of the body is maintained at this constant value. If an abnormal amount of water vapor is present in the air, the evaporation of moisture from the skin takes place very slowly, and bodily discomfort follows. Moreover, when the air is perfectly still, that portion of the air in contact with the body tends to become saturated with moisture, and evaporation diminishes or ceases entirely; hence the relief that comes from keeping the air in motion, as with an electric fan.

In general, a moisture content of about 70 per cent of that required for saturation is most conducive to comfort. The volume of fresh air necessary for good ventilation varies greatly with conditions, but in general may be said to be about 1 cu. m. per minute for each person.



**The properties of air.** Inasmuch as air is composed principally of a mixture of oxygen and nitrogen (elements which have already been discussed), its properties may be inferred largely from those of the two gases named. One liter weighs 1.2930 g.

**Liquid air.** We have seen (p. 123) that air, like all other gases, can be liquefied by the combined effect of pressure and

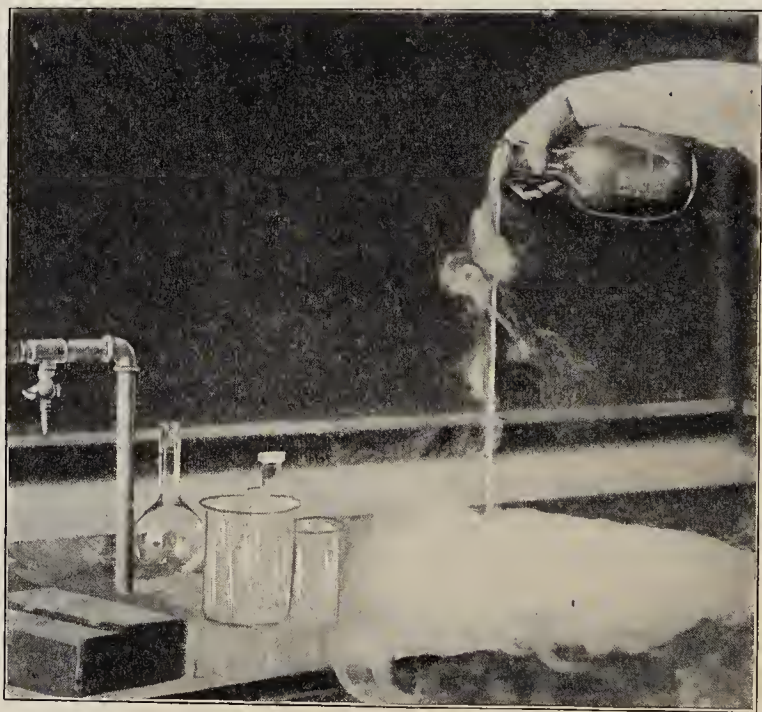


FIG. 69. Pouring liquid air from a thermos bottle

low temperature. Liquid air (Fig. 69) is essentially a mixture of liquid nitrogen (boiling point,  $-195.8^{\circ}$ ) and liquid oxygen (boiling point,  $-183^{\circ}$ ); hence if liquid air is allowed to evaporate, the nitrogen tends to vaporize first. Advantage is taken of this difference in boiling points to separate the oxygen and nitrogen from each other, and the method serves as a commercial one for obtaining the two gases. Liquid air is also employed when very low temperatures are desired. It may be kept for several hours by storing it in Dewar flasks (Fig. 50).

The extremely low temperature of liquid air may be inferred from the fact that mercury, when cooled by it, is frozen to a mass so hard that it may be used for driving nails.

### EXERCISES

1. What essential constituent of the air is found in larger quantities in manufacturing districts than in the open country?

2. Can you suggest any reason why the growth of clover in a field improves the soil?

3. When ice is placed in a vessel containing liquid air, the latter boils violently. Explain.

4. Does an electric fan lower the temperature of a room? Why is relief obtained by its use?

5. Would combustion be more intense in liquid than in gaseous air?

6. Taking the volumes of the oxygen and nitrogen in 100 volumes of air as 21 and 78 respectively, calculate the percentages of these elements present by weight.

7. Assuming that dry wood contains 40 per cent of carbon, all of which originally came from carbon dioxide in the air, what weight of  $\text{CO}_2$  would have to be absorbed by a plant to make 500 g. of wood?

8. Copper combines with oxygen in accordance with the equation  $2\text{Cu} + \text{O}_2 \longrightarrow 2\text{CuO}$ . What weight of copper would be required to combine with the oxygen in 5 liters of dry air?

9. A tube containing calcium chloride was found to weigh 30.1293 g. A volume of air which weighed 15.2134 g. was passed through the tube, after which the weight of the tube was found to be 30.3405 g. What was the percentage of moisture present in the air?

10. 10 liters of air measured at  $20^\circ$  and 740 mm. passed through lime-water caused the precipitation of 0.0102 g. of  $\text{CaCO}_3$ . Find the number of volumes of carbon dioxide in 10,000 volumes of the air.

## CHAPTER XIV

### SOLUTIONS

**Introduction.** We make such constant use of solutions in everyday life long before we begin the study of chemistry that we are apt to think little about them. We stir sugar into our tea or coffee; we see a glass of soda water bubble, or effervesce, and assume that the escaping gas was dissolved in the water; we have been told many times that the water of the ocean differs from fresh water because of a much larger amount of salts dissolved in it. By patient study much definite information about solutions has been gained, and we must now give the subject our attention.

**Solute and solvent.** A solution may always be regarded as made up of two components: (1) the *solute*, or the substance which undergoes solution, such as the sugar, the gas, and the salts in the examples just given; (2) the *solvent*, or the medium in which the solute is dissolved. In the solutions with which we are most familiar, water is the solvent.

**Nature of solutions.** In an earlier chapter a distinction was made between a mixture and a compound. In a mixture particles of different properties may be observed, so that it is not entirely uniform throughout, or is not *homogeneous* in character. *A solution differs from a mixture in being completely homogeneous.* In a compound every smallest particle is identical in composition, so that we may give a definite formula to the compound. In a solution we may add a small amount of solute or a much larger amount, and vary the composition of the solution between wide limits. *A solution differs from a compound in that its composition can be varied*

*between definite limits.* These two characteristics may be so stated as to form a definition of a solution, and we may say that *a solution is a body, homogeneous in character, whose composition may be varied at will between certain limits.* From this definition we see that what is commonly called a mixture of two liquids, such as alcohol and water, is really a solution.

**Solution a fourth state of matter.** When we dissolve salt in water the question may occur to us, Is the salt still a solid or has it become a liquid or a gas? Certainly it cannot still be a solid, for the entire solution is completely liquid. It is equally hard for us to think of the salt as a liquid or a gas, for the temperature of the solution is far below that of the melting point of salt. We therefore consider the dissolved salt to be in a state different from any of these, constituting a fourth state of matter called the *dissolved state*. We shall see later on that there is a fifth state known as the colloidal state.

**Varieties of solutions.** While we ordinarily think of solutions as being formed in a liquid solvent, the definition that we have framed does not require this. Nor is the solute always a solid. One gas may dissolve another gas, or it may dissolve a liquid (as when water evaporates into air). A solid may dissolve a gas, a liquid, or even another solid. For example, brass is a solid solution of zinc in copper. The most familiar types of solutions, however, are solutions of a gas, a liquid, or a solid in a liquid.

### SOLUTIONS OF GASES IN LIQUIDS

We have seen that oxygen, hydrogen, nitrogen, and carbon dioxide are slightly soluble in water. Accurate study has led to the conclusion that all gases are soluble to some extent, not only in water but in many other liquids. The amount of a gas which will dissolve in a liquid depends upon a number of conditions, and these can best be understood by

supposing a vessel to be filled with the gas (*B*, Fig. 70) and inverted over the liquid *A*. Under these circumstances the

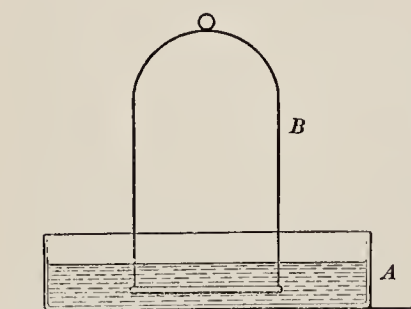


FIG. 70. The solubility of a gas inclosed over water

gas cannot escape or become mixed with another gas.

**Factors affecting the solubility of gases.** A number of factors affect the solubility of a gas in a liquid.

**1. Nature of the gas.** Other conditions being equal, each gas has its own peculiar solubility, just as it has its own special weight or odor. The solubility of gases varies between wide limits, as will be seen from the following table, which gives the volumes of some well-known gases that will dissolve in 1 liter of water under standard conditions.

#### SOLUBILITY OF GASES IN ONE LITER OF WATER

NAME OF GAS	VOLUME ABSORBED AT 0° AND UNDER 760 MM. PRESSURE
Ammonia . . . . .	1298.9 l.
Hydrogen chloride . . . . .	506.0 l.
Sulfur dioxide . . . . .	79.79 l.
Hydrogen sulfide . . . . .	4.37 l.
Carbon dioxide . . . . .	1.713 l.
Oxygen . . . . .	0.0496 l.
Nitrogen . . . . .	0.0233 l.
Hydrogen . . . . .	0.0214 l.

It will be noted that some gases, such as ammonia, are extremely soluble. This is due to the fact that some of the gas combines with the water to form a soluble compound.

**2. Nature of the liquid.** The character of the liquid has much influence upon the solubility of a gas. Each liquid, such as water, alcohol, or ether, has its own peculiar solvent



power. From the solubility of a gas in water no prediction can be made as to its solubility in other liquids.

3. *Effect of pressure; the law of Henry.* In 1803 the Englishman Henry studied the effect of pressure upon the solubility of a gas. He reached the following conclusion, known as the law of Henry. *Increase of pressure always increases the weight of gas going into solution, the increase being proportional to the pressure.* If 1 g. of a gas dissolves in 100 cc. of water at atmospheric pressure, 2 g. will dissolve under 2 atmospheres, provided the temperature remains constant. Under high pressure large quantities of a gas may be dissolved in a liquid. In such solutions, when the pressure is removed, that fraction of the gas escapes that was held in solution by the increased pressure.

4. *Influence of temperature.* In general, the lower the temperature of the liquid, the larger the quantity of gas which it can dissolve. Thus, 1 liter of water at  $0^{\circ}$  will dissolve 0.0496 liters of oxygen; at  $50^{\circ}$ , 0.01837 liters; at  $100^{\circ}$ , none at all. While most gases can be driven from a liquid by boiling the solution, some cannot. For example, it is not possible to expel hydrogen chloride from its solution completely by boiling.

#### SOLUTIONS OF LIQUIDS IN LIQUIDS

Some liquids mix with each other in all proportions and form a perfect solution. This is true of alcohol and water as well as of water and the familiar chemicals known as sulfuric acid and nitric acid. In other cases a liquid becomes saturated with another liquid, and if more of the latter is added it forms a second liquid layer. Each layer is then a saturated solution. Thus, a few cubic centimeters of chloroform will dissolve in 100 cc. of water, but if much more than that is added, we get two layers: the lower (heavier) layer consists of chloroform saturated with water; the upper (lighter) is water saturated with chloroform. In still other cases, as of kerosene and water, each liquid is practically insoluble in the other.

## SOLUTIONS OF SOLIDS IN LIQUIDS

A solid dissolved in a liquid is by far the most familiar type of solution. In the following discussion it should be remembered that we are dealing with true solutions only. Thus, it is sometimes said that zinc dissolves in hydrochloric acid. In this case, however, the solution is preceded by an undoubted chemical reaction whereby the zinc is converted into zinc chloride, and it is this compound which is obtained when the solution is evaporated to dryness. With solutions such as we are now considering, evaporation leaves the solute in its original chemical condition.

**Factors affecting the solubility of a solid.** The solubility of a solid in a liquid depends upon several factors.

1. *Nature of the solid.* Other conditions being the same, solids vary greatly in their solubility in liquids (see table on the following page).

No solids are absolutely insoluble, but the amount dissolved may be so small as to be of no significance for most purposes. Thus, barium sulfate, one of the most insoluble of common substances, dissolves in water to the extent of about 1 part in 400,000.

2. *Nature of the solvent.* Liquids vary much in their power to dissolve solids. Some are said to be good solvents, since they dissolve a great variety of substances and considerable quantities of them; others have small solvent power, dissolving few substances, and those to only a slight extent. Broadly speaking, water is the most general solvent, and alcohol is perhaps second in solvent power.

3. *Pressure.* Very great increase in pressure has a marked effect upon the solubility of a solid in a liquid, but small changes, such as those due to atmospheric pressure, have little effect.

4. *Temperature.* The weight of a solid which a given liquid can dissolve varies with the temperature. Usually it increases

rapidly as the temperature rises, so that the boiling liquid dissolves a much greater weight than the cold liquid will dissolve. In some instances, as in the case of sodium chloride (common salt) dissolved in water, the temperature has little influence upon the solubility, and a few solids such as calcium hydroxide (slaked lime) are more soluble in cold water than in hot. The following examples will serve as illustrations:

TABLE OF SOLUBILITY OF SOLIDS

SUBSTANCE	FORMULA	WEIGHT DISSOLVED BY 100 CC.OF WATER AT		
		0°	20°	100°
Calcium chloride . . .	$\text{CaCl}_2$	59.50 g.	74.5 g.	159.0 g.
Sodium chloride . . .	$\text{NaCl}$	35.70 g.	36.0 g.	39.80 g.
Potassium nitrate . . .	$\text{KNO}_3$	13.30 g.	31.6 g.	246.0 g.
Copper sulfate . . . .	$\text{CuSO}_4$	14.30 g.	21.7 g.	75.4 g.
Calcium sulfate . . . .	$\text{CaSO}_4$	0.759 g.	0.203 g.	0.162 g.
Calcium hydroxide . .	$\text{Ca(OH)}_2$	0.185 g.	0.165 g.	0.077 g.

**Saturated solutions.** When a lump of sugar is placed in a small beaker and covered with water, as represented in Fig. 71, it gradually diminishes in size and passes into solution, particles leaving it and diffusing through the solvent. If there is enough sugar, and a long enough time elapses, the concentration of the sugar in the solution reaches a definite limiting value, and we say that the sugar ceases to dissolve and that the solution is *saturated*. There is good reason for thinking that particles continue to leave the lump, but that an equilibrium has been reached, the rate of departure of the particles being equal to the rate of the return of others from the solution. *A saturated solution may therefore be defined as one which is in equilibrium with excess of the undissolved solute.*

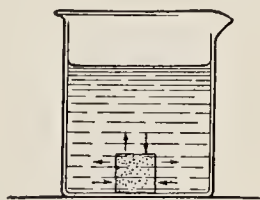


FIG. 71. Diagram illustrating the equilibrium of a saturated solution

**Rate of solution.** Unless the solution is constantly stirred it takes a long time to bring about saturation. The portion of the liquid in immediate contact with the solid dissolves the solid rapidly at first, then more and more slowly as saturation is approached. Meanwhile the solute makes its way, or *diffuses*, very slowly into the portions of the solvent not in contact with the solid. Thus, if some crystals of a highly colored substance, such as potassium permanganate, are placed in the bottom of a tall vessel full of water, it will take weeks or even months for the solution to become uniformly colored. Vigorous stirring rapidly brings all the solvent into contact with the solid, and approximate saturation is reached in a few minutes; but even then *complete* equilibrium is reached very slowly at constant temperature.

**Separation of solids from their solutions.** When any given solid separates from its solution, it is usually deposited in crystalline form, each solid having its own definite form. This process is often employed to purify solids, such solvents being selected as will retain the impurities in solution. The separation of a solid from its solution is usually brought about in one of two ways: (1) The solvent may be saturated with the solid at room temperature and the resulting solution set aside. The solvent gradually evaporates and the solid is slowly deposited. (2) Most solids are much more soluble at high temperatures than at low; consequently, if a solution of such a solid is saturated at a high temperature and set aside to cool, then, in most cases (see next paragraph), all the solid in excess of the quantity required to saturate the solution at the lower temperature crystallizes out.

**Supersaturated solutions.** When a solution, saturated at a given temperature, is allowed to cool, it sometimes happens that no solid crystallizes out, although the solid may be much less soluble in the cold than in the hot liquid. This is very likely to occur when the solution is rather viscous, like sirup, and is not disturbed in any way. Such a solution is said to be *supersaturated*. That this condition is unstable can be shown by adding a crystal of the solid to the solution. All



the solid in excess of the quantity required to saturate the solution at this temperature will at once crystallize out (Fig. 72). Supersaturation may also be overcome in many cases by vigorously shaking or stirring the solution.

**Solubility curves.** As a rule, the solubility of a solute does not vary with temperature in any regular manner, so we can best represent the facts in a given case by a curve, plotting the temperature as the abscissa and the number of grams dissolved by 100 grams of water as the ordinate. The diagram (Fig. 73) shows a few typical curves. It will be seen that some substances are very soluble, while others are not. The solubility of some increases rapidly with the increase in temperature, while with others the increase is small.

**Gram-molecular or molar solutions.** In stating the concentration

of a solution we may obviously make use of the percentage system, but it is often much better to state the number of formula weights or molecular weights (measured in grams) which a given volume of the solution contains. *When as many grams of a substance as there are units in its molecular weight are dissolved so as to make a liter of solution, it is said to be a gram-molecular or molar solution.* Thus, a gram-molecular solution of sodium chloride ( $\text{NaCl}$ ) contains  $22.997 + 35.457$  g., or  $58.454$  g., of the solid in 1 liter of the solution.

**Raoult's laws.** A number of generalizations, or laws, have been formulated which describe the effect produced upon the various properties of a solvent by gram-molecular quantities of various solutes. Three of these, known as Raoult's laws (formulated in 1883), are of especial interest to us.

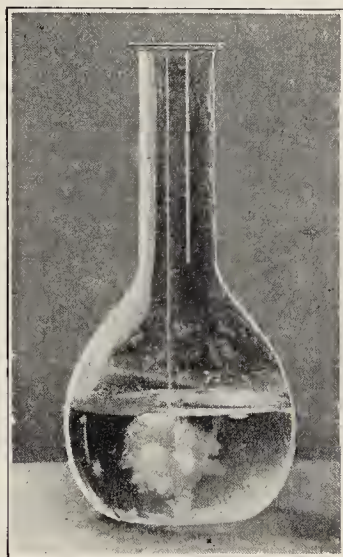


FIG. 72. The rapid growth of a crystal suspended in a supersaturated solution



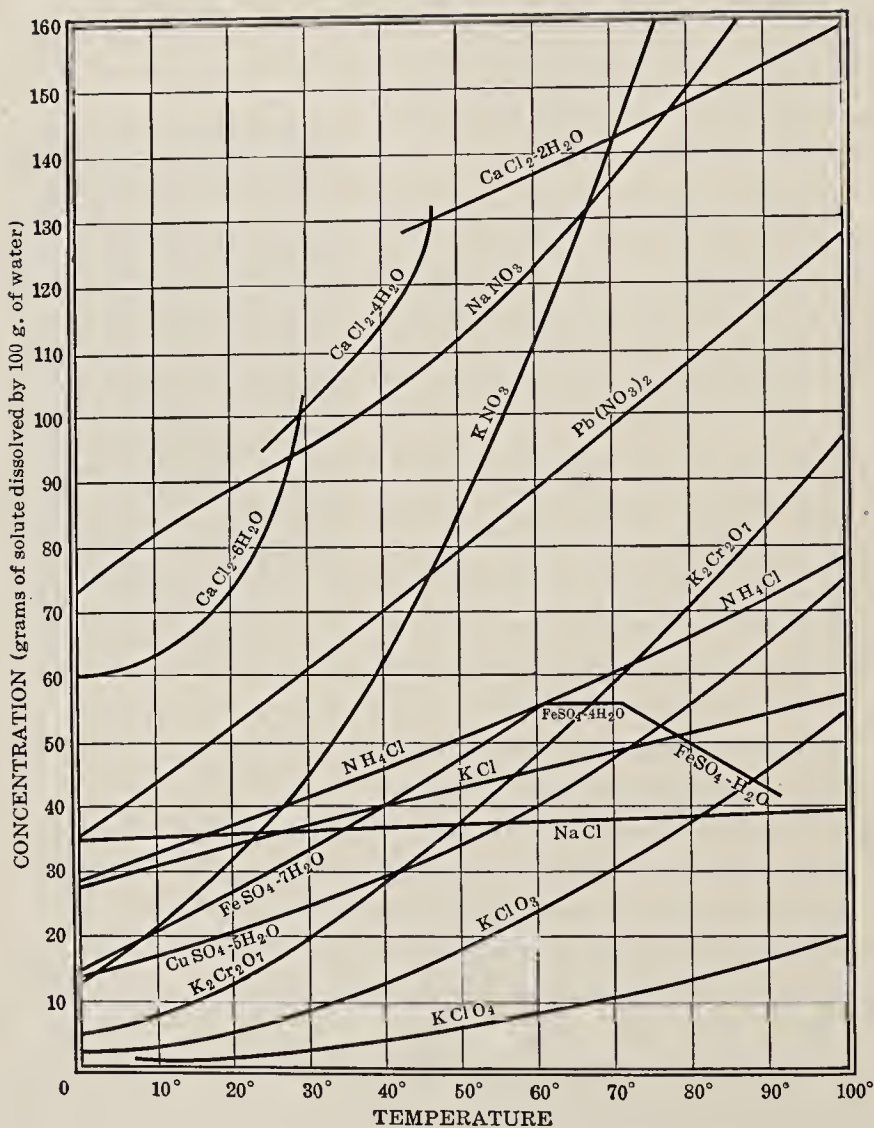


FIG. 73. Solubility curves of a number of compounds showing the number of grams of each of the compounds that will dissolve in 100 g. of water at different temperatures

1. *The effect of a solute upon the boiling point of a solvent.*

The boiling point of a liquid is raised by the presence of a dissolved solid, and in general *the extent of rise in boiling point is proportional to the gram-molecular concentration of the solution.* In other words, if we have two compounds, *A* with a molecular weight of 100 and *B* with a molecular weight of 200, then 100 g. of *A* dissolved in 1 liter of water will produce the same rise in the boiling point of the water as will 200 g. of *B*. It appears, therefore, that it is not the weights of the molecules of the solute, but their number alone, that determines the change in boiling point of the solvent.

2. *The effect of a solute upon the freezing point of a solvent.*

The freezing point of a liquid is lowered by the presence of a dissolved solid, and in general *the extent of the lowering of the freezing point is proportional to the gram-molecular concentration of the solution.*

3. *The effect of a solute upon the vapor pressure of a solvent.*

The vapor pressure of a liquid is lowered by the presence of a dissolved solid. *The extent of the lowering of the vapor pressure is proportional to the gram-molecular concentration of the solution,* and is independent of the character of the dissolved solute.

**Limitation of Raoult's laws.** While Raoult's laws apply very accurately to a great variety of solutes dissolved in many different solvents, it has been found that they do not apply to compounds whose solutions conduct the electric current. It is of special interest to note that in all solutions that are good conductors the effect of the solute on the boiling point or on the freezing point of the solvent *is much greater* than it would be if Raoult's laws were to hold good. The reasons for this will be discussed in a later chapter.

**Deliquescence.** If we expose a crystal of a very soluble solid to moist air, the crystal soon becomes visibly moist and in time completely dissolves. This process is called *deliquescence*, and the solid is said to be *deliquescent*. Crystallized calcium chloride is a good example of a deliquescent compound.

**Explanation of deliquescence.** The explanation of deliquescence affords an interesting application of the third of Raoult's laws. The vapor pressure of water at ordinary temperatures ( $20^{\circ}$ ) is 17.51 mm. As a rule the air is about two thirds saturated with water vapor, so that the partial pressure of the water vapor in the air is about 12 mm.

If we dissolve large quantities of a very soluble solid in water, we can easily reduce the vapor pressure of the solution below 12 mm. Such a solution, exposed to the air, will not evaporate, but, on the contrary, will absorb water from the air and become more dilute.

Now all solids tend to condense a film of moisture upon their surface. If, therefore, we expose a crystal of a very soluble solid to moist air, this surface film becomes saturated with the solid, and the solution has a vapor pressure below that of the partial pressure of the water vapor in the air. It therefore absorbs water from the air, diluting the solution. More solid then dissolves, and the cycle continues until all the solid has dissolved. From this explanation it will be seen that *any very soluble solid must be deliquescent*.

**Osmotic pressure.** We have seen that when a soluble solid is placed in a solvent, it gradually dissolves and its molecules diffuse through the entire body of the solvent. If we devise a method for stopping this diffusion, we find that a very great pressure develops, known as *osmotic pressure*. This can be demonstrated by means of a so-called *semipermeable* membrane, — for example, parchment paper or certain animal membranes such as bladder or sausage casings. Water passes readily through these membranes, but most dissolved solutes cannot.

If we fill a bladder with a solution of sugar or salt or alcohol, tie it tightly, and immerse it in water, none of the solute can pass into the surrounding water, but the water passes through the membrane readily. As a result the external water flows through the membrane into the solution, and the bladder swells up until it bursts.

The same effect can be shown more easily as follows: A piece of parchment paper is tied tightly over the bell of a

long-stemmed funnel or thistle tube (Fig. 74); the bell of the funnel is filled with a solution, say of sugar, and the bell is then immersed in water. The water flows through the membrane into the solution, increasing its volume (and diluting the solution) so that it rises in the stem of the tube like mercury in a thermometer.

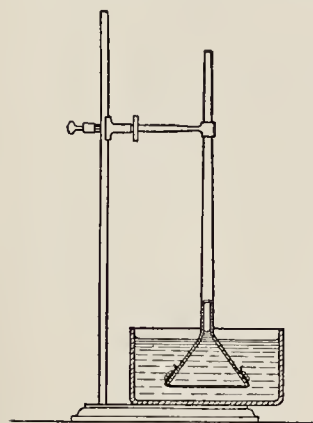


FIG. 74. Apparatus that shows osmotic pressure

It has been found that the force of osmotic pressure, measured by the rise in the funnel stem, *is proportional to the gram-molecular concentration of the solute and is independent of its nature.* This statement, like those given above in reference to the rise in boiling point and the lowering of the freezing point, do not apply to compounds whose solutions conduct the electric current.

**Electrolysis of solutions.** Pure water does not appreciably conduct the electric current; nor do many solutions, such as sugar dissolved in water. If, however, certain compounds such as common salt or hydrochloric acid are dissolved in the water, the resulting solutions are found to be good conductors but do not obey Raoult's laws. Such compounds are called *electrolytes*. *When the current passes through a solution of an electrolyte, some chemical change always takes place. This change is called electrolysis.*

The general method used in the electrolysis of a solution is illustrated in Fig. 75. Two plates or rods, *A* and *B*, made of suitable material, are connected with the wires from a battery (or dynamo) *C* and dipped into the electrolyte, as shown in the figure. These plates or rods are called *electrodes*. The electrode *B* connected with the negative pole of the battery is the

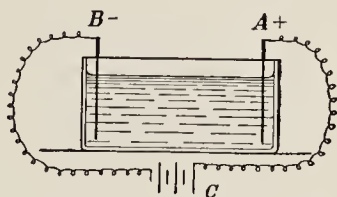


FIG. 75. Diagram to illustrate the electrolysis of a solution



negative electrode, or *cathode*, while that connected with the positive pole *A* is the positive electrode, or *anode*. The particular form of apparatus used varies in individual cases; thus, in the electrolysis of water the electrodes are so arranged (Fig. 5) that the oxygen and hydrogen evolved may be collected.

In this way the electric current is utilized in bringing about chemical changes. It is being used more and more in the commercial preparation of many of the metals and their compounds. Thus, the metal aluminum, used so largely in the construction of automobiles and culinary vessels, is obtained entirely by electrolysis. By the same process copper is purified and various objects are plated with gold and silver (electroplating).

### EXERCISES

1. Distinguish clearly between the following terms: *electrolysis*, *electrolyte*, *cathode*, *anode*, *solute*, *solvent*, *solution*, *saturated solution*, and *super-saturated solution*.

2. Why does the water from some natural springs effervesce?

3. Why does not the water of the ocean freeze?

4. Why does shaking or stirring make a solid dissolve more rapidly in a liquid?

5. Why will vegetables cook faster when boiled in strong salt water than when boiled in ordinary water?

6. How do you explain the foaming of soda water?

7. Account for the fact that sugar sometimes deposits from sirups, even when no evaporation has taken place.

8. Is it correct to define a saturated solution of any solid in a liquid as "one that contains all the solid the liquid will dissolve"?

9. (a) Why is alcohol added to the water used in the radiator of an automobile in cold weather? (b) Suggest some other substance that could be used in place of alcohol.

10. Wood alcohol ( $\text{CH}_3\text{OH}$ ), grain alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ), and glycerin ( $\text{C}_3\text{H}_5(\text{OH})_3$ ) are all soluble in water in all proportions. If you had 1 kg. of each, which would be the most effective for use to prevent the freezing of water in the radiator of an automobile?



**11.** 100 g. of sodium chloride was dissolved in sufficient water to give 1500 cc. of solution. What was the molar concentration?

**12.** 200 g. of potassium nitrate was dissolved in 120 cc. of boiling water and the solution cooled to 20°. What weight of potassium nitrate separated?

**13.** A saturated solution of each of the compounds, potassium nitrate, sodium chloride, and calcium hydroxide, was prepared by heating the solids with 1000 cc. of water. How would the lowering of the temperature affect each solution?

**14.** 10 g. of common salt was dissolved in water and the solution evaporated to dryness; what weight of solid was left? 10 g. of zinc was dissolved in sulfuric acid and the solution evaporated to dryness; what weight of solid was left?

## CHAPTER XV

### CHLORINE ; HYDROGEN CHLORIDE ; HYDROCHLORIC ACID ; ACIDS

● **Introductory.** We have now reached a point in our study when it becomes necessary to turn our attention to the group of compounds known as *acids*. Of these, *hydrochloric acid* is perhaps the simplest and most familiar, and a study of this one acid will bring into view the most characteristic properties of acids as a class of compounds.

Hydrochloric acid is an aqueous solution of a compound of the two elements hydrogen and chlorine. We have already studied hydrogen, and it is advisable for us to become acquainted with chlorine as a preliminary to our study of hydrochloric acid.

**Properties of chlorine.** During the World War our newspapers and magazines had much to say concerning chlorine, for it was the first substance used by the Germans as a poison gas. Like most of the elements so far studied, chlorine is a gas; but, unlike them, it has a greenish-yellow color and a peculiar suffocating odor. When inhaled, even in small quantities, it acts injuriously upon the throat and lungs, producing many of the symptoms of a hard cold, while in larger quantities it may have serious or even fatal consequences. On this account great care must be taken in working with this gas in the laboratory. Chlorine is a heavy gas, being nearly 2.5 times as heavy as air. One volume of water under ordinary conditions dissolves 3 volumes of the gas.

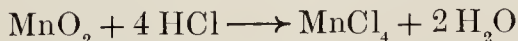
**Occurrence.** Chlorine does not occur free in nature, but its compounds are widely distributed. It is found in combination with the metals in the form of *chlorides*, those of sodium,

magnesium, and potassium being the most abundant. All salt water contains these chlorides, particularly the one known as *sodium chloride* (NaCl) or *common salt*. Very large beds of chlorides are found in many parts of the world. About 2 parts in every 1000 of the material of the world is chlorine.

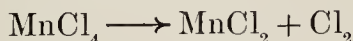
**Historical.** Chlorine was discovered by Scheele (Fig. 39) in 1774. For years after its discovery it was thought to be a compound of hydrochloric acid and oxygen, but in 1810 the English chemist Sir Humphry Davy (Fig 76) proved it to be an element and gave it the name which it now bears.

**Preparation.** Three methods for preparing chlorine will be described, two of which are laboratory methods and the third a commercial method.

1. **First laboratory method.** A common method for preparing chlorine in the laboratory consists in warming a mixture of hydrochloric acid and manganese dioxide ( $\text{MnO}_2$ ). The hydrogen of the acid and the manganese of the dioxide exchange places, forming manganese tetrachloride ( $\text{MnCl}_4$ ), thus:



The resulting manganese tetrachloride, however, is unstable and breaks down as fast as formed into manganous chloride ( $\text{MnCl}_2$ ) and chlorine, thus:



This method led Scheele to the discovery of chlorine.

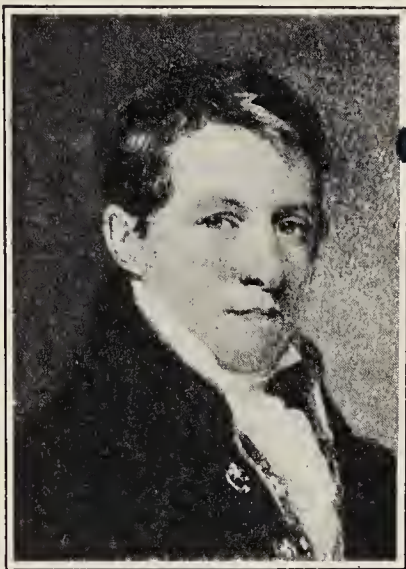


FIG. 76. Sir Humphry Davy  
(1778-1829)

A distinguished English scientist who proved that chlorine is an element and first isolated the metals sodium and potassium

**Laboratory apparatus.** The manganese dioxide and the hydrochloric acid are brought together in a flask *A* (Fig. 77), and a gentle heat is applied. The chlorine set free escapes through the tube *B* and is collected in the cylinder *C* by displacement of air, the color indicating when the cylinder is filled.

Instead of using hydrochloric acid in the preparation of chlorine, it serves just as well to use a mixture of sodium chloride and sulfuric acid, since these two react to form hydrochloric acid. In this case the complete reaction is expressed by the equation



**2. Second laboratory method.** A second laboratory method, often used when a limited supply of chlorine is desired, consists in oxidizing hydrochloric acid according to the equation



Free oxygen may be used, but the reaction is very slow. The use of suitable catalytic agents (such as copper sulfate) increases the yield, but it is much more convenient to substitute an oxidizing agent for the free oxygen. The best oxidizing agent for the purpose is the purple-black solid having the formula  $\text{KMnO}_4$  and known as *potassium permanganate*.

The complete reaction is complex and will be explained more fully in a later chapter; for the present it is only necessary to remember that in a general way the chlorine is liberated according to the above equation, the oxygen being derived from the potassium permanganate. While this method of preparation is somewhat more expensive than the first method, it nevertheless has an advantage in that no heat is required.

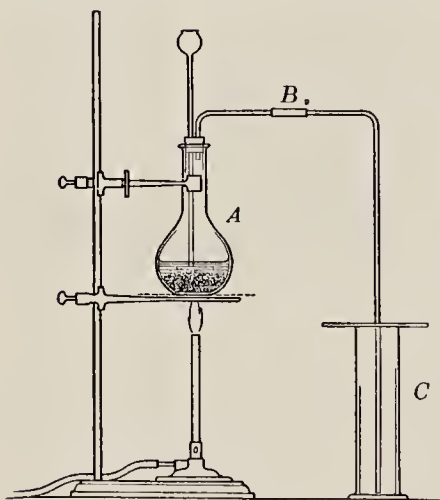


FIG. 77. Preparation of chlorine by the action of hydrochloric acid on manganese dioxide

**Laboratory apparatus.** To obtain chlorine in the laboratory by this method the potassium permanganate is placed in a flask *A* (Fig. 78), and a mixture of equal volumes of concentrated hydrochloric acid and water is added, drop by drop, from a funnel *B* provided with a stopcock so that the flow of the liquid can be regulated. (Such a funnel is called a *separatory funnel*.) The reaction takes place at once, and the chlorine evolved through *C* is collected by displacement of air. If a high degree of purity is desired, the gas should be bubbled through sulfuric acid.

3. **Commercial method.** When an electric current is passed through an aqueous solution of sodium chloride (Fig. 75), chlorine is evolved at the anode and sodium is set free at the cathode. The sodium, however, as fast as liberated, reacts with the water present, forming hydrogen, which is evolved at the cathode, and sodium hydroxide ( $\text{NaOH}$ ), which remains dissolved in the water (p. 43). *The products of the reaction, therefore, are chlorine, hydrogen, and sodium hydroxide.* All the chlorine prepared for commercial purposes in the United States is obtained in this way. The method has advantages in that sodium chloride is cheap, and the sodium hydroxide formed in the process has many commercial uses. The chlorine so obtained is either used at the plant for bleaching or is compressed in strong iron cylinders and shipped in this form; or it is passed into slaked lime, forming the solid known as *chloride of lime* or *bleaching powder*, which can be easily shipped and from which the chlorine can be recovered as needed.

The apparatus in which the electrolysis of the salt is carried out is known as a *cell*. There are several different kinds of cells, each being designated by the name of its inventor.

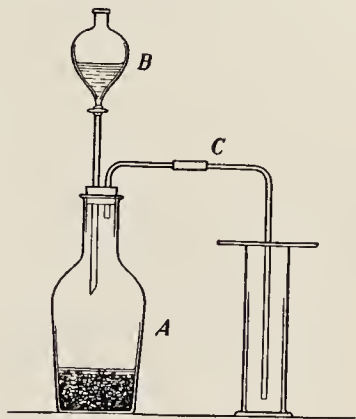


FIG. 78. Preparation of chlorine by the action of hydrochloric acid on potassium permanganate



The chief difficulty in preparing chlorine by electrolysis consists in keeping apart the chlorine and sodium hydroxide formed, for if they come together they react with each other and the chlorine enters into combination. This difficulty is overcome by separating the anode and cathode compartments by a porous diaphragm. The Nelson cell (Fig. 79) illustrates the general process involved. In this cell the anode *B, B* is composed of rectangular pieces of carbon, while the cathode *C* is made of perforated steel. Just

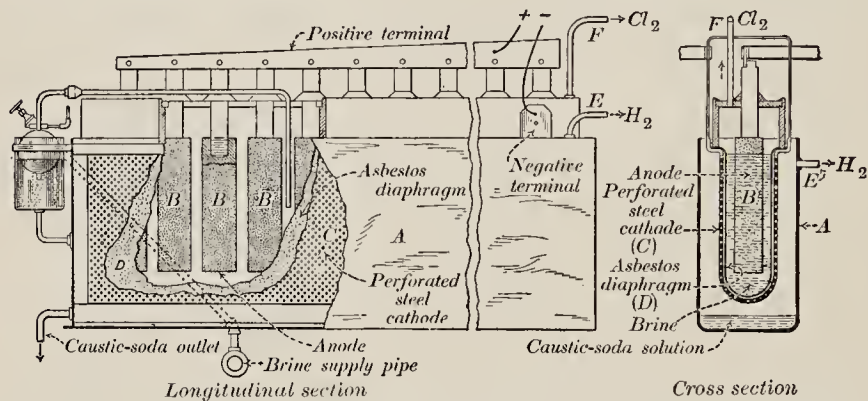


FIG. 79. Longitudinal section and cross section of a Nelson cell for the production of chlorine on a large scale

inside the cathode is an asbestos diaphragm *D*. The anode compartment is kept filled with brine, as shown in the figure, and the electric current is connected at the points indicated. The sodium chloride is decomposed, the chlorine liberated at the anodes escaping through the pipe *F*. The sodium is liberated at the cathode and combines with the water present to form sodium hydroxide, which remains dissolved in the water, and hydrogen, which escapes through the pipe *E*. The solution of sodium hydroxide, containing also some sodium chloride, runs through the perforations in the cathode and is drawn off and evaporated. The sodium chloride present, being much less soluble than the sodium hydroxide, separates first and is removed. The remaining solution, upon evaporation, yields the solid sodium hydroxide. The Nelson cell is about 10 ft. in length and produces 60 lb. of chlorine and 65 lb. of sodium hydroxide every twenty-four hours.

**Chemical conduct.** At ordinary temperatures chlorine is far more active chemically than any element so far considered;

indeed, it is one of the most active of all elements. Its activity may be described under a number of distinct headings.

1. *Action on elements other than hydrogen.* Many of the elements combine directly with chlorine even at ordinary temperatures. Thus, phosphorus burns in a current of the gas, while antimony and arsenic, in the form of a fine powder, at once burst into flame when dropped into jars of the gas (Fig. 80). When a strip of copper foil heated to redness is dropped into chlorine,

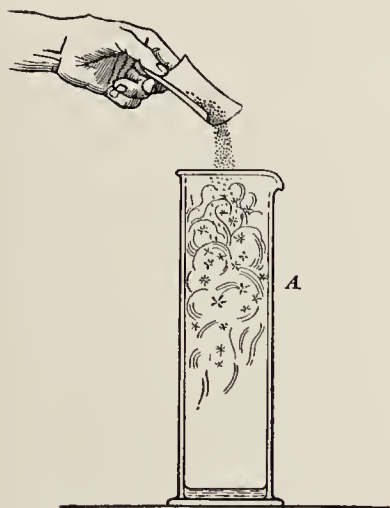


FIG. 80. The burning of powdered metals in chlorine gas

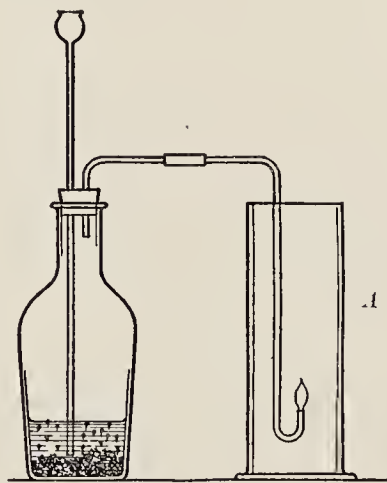


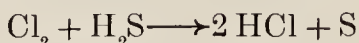
FIG. 81. The burning of a jet of hydrogen in an atmosphere of chlorine

the two elements unite with incandescence. Even inactive metals like gold and platinum are tarnished by the gas. The compounds formed by the union of chlorine with another element are called *chlorides* and constitute a very important group. Common salt, for example, is chloride of sodium ( $\text{NaCl}$ ).

2. *Action on hydrogen.* Chlorine has a strong affinity for hydrogen, uniting with it to form gaseous hydrogen chloride ( $\text{HCl}$ ). A jet of hydrogen burning in the air continues to burn when introduced into a jar of chlorine, giving a somewhat luminous flame (Fig. 81). A mixture of the two gases explodes violently when a spark is passed through it or when

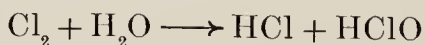
it is exposed to bright sunlight. In the latter case it is the light and not the heat which starts the action.

3. *Action on compounds of hydrogen.* Not only will chlorine combine directly with free hydrogen, but it will often abstract the element from its compounds. Thus, when chlorine is passed into a solution of hydrogen sulfide, the chlorine combines with the hydrogen, while sulfur is set free in accordance with the following equation :

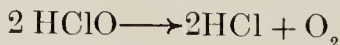


The same tendency is very strikingly seen in the action of chlorine upon turpentine. The latter substance is largely made up of compounds which have the composition represented by the formula  $\text{C}_{10}\text{H}_{16}$ . When a strip of paper moistened with warm turpentine is placed in a jar of chlorine, the hydrogen of the turpentine combines with the chlorine to form hydrogen chloride, and the carbon is set free in the form of a black solid.

4. *Action on water.* The reaction between chlorine and water is a special instance of the action of chlorine upon compounds containing hydrogen, and is of great importance, since the use of chlorine as a bleaching agent is based primarily upon it. When the chlorine is passed into water, both hydrochloric acid and hypochlorous acid ( $\text{HClO}$ ) are formed :



The hypochlorous acid, however, is a very unstable compound and breaks down, slowly in the dark but rapidly in the sunlight, as follows :



The decomposition of water through the action of chlorine is also greatly increased in the presence of some substance which combines with the oxygen as fast as it is set free. Consequently a solution of chlorine in water is a good oxidizing agent, and, indeed, it is often used as such.

**Effect of sunlight.** The effect of sunlight in increasing the action of chlorine upon water may be shown in the following way: If a long tube of rather large diameter is filled with a saturated solution of chlorine in water and inverted in a vessel of the same solution (as shown in Fig. 82), and the apparatus is placed in bright sunlight, bubbles of gas will soon be seen to rise through the solution and collect in the tube. An examination of this gas will show that it is oxygen.

**5. Action on color substances; bleaching action.** If strips of brightly colored cloth or some highly colored flowers are placed in *dry* chlorine, no marked change in color is noticed, as a rule. If, however, the cloth and flowers are first moistened, the color rapidly disappears, or, in other words, the objects are *bleached*. Evidently the moisture as well as the chlorine is concerned in the action. A study of the case proves that the chlorine sets the oxygen free from the water, as shown above, and the oxygen so liberated oxidizes the color substance (dye), converting it into a colorless compound. It is evident from this explanation that chlorine will bleach only those substances which are changed into colorless compounds by oxidation. It has no action on such color substances as carbon, and hence does not affect printer's ink made from carbon. It cannot be used for bleaching certain substances like silk and straw, since it injures the fabric.

Bleaching is an important process in connection with many industries. Thus, the various kinds of fabrics woven from vegetable fibers, such as flax and cotton, are always more or less colored; hence bleaching is necessary if a white fabric is desired. This was formerly accomplished by spreading the cloth on plots of grass and exposing it to air and sunlight, but the process was very slow. The same results are now obtained in a short time by the use of chlorine.

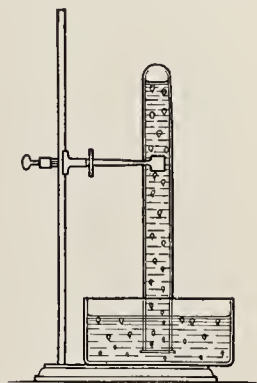


FIG. 82. Decomposition of water by chlorine in the sunlight



**Illustration of bleaching.** Fig. 83 illustrates the bleaching action of chlorine. Strips from the same piece of cloth are suspended in three jars, of which the first contains air, the second *dry* chlorine, and the third *moist* chlorine. It will be noted that dry chlorine has almost no bleaching action, while the moist chlorine has partially removed the color.



FIG. 83. Bleaching strips of colored cloth by chlorine

#### 6. Action as a germicide.

Chlorine has marked germicidal properties, and the free element, as well as the compounds from which it is easily liberated, are used as disinfectants. During the war it was noticed that the soldiers employed in the chlorine plants largely escaped influenza. Experiments conducted since that time seem to indicate that a very small percentage of chlorine in the air may turn

out to be very effective in preventing a variety of germ diseases.

**Uses.** The normal production of chlorine in the United States amounts to nearly 500 tons daily. Most of this is used in bleaching fabrics and especially in the bleaching of wood pulp, from which paper is made. It is also used in the purification of water (Chapter XXXVIII) and in making *bleaching powder* and such compounds as chloroform ( $\text{CHCl}_3$ ) and carbon tetrachloride ( $\text{CCl}_4$ ). Increasing quantities are now compressed in strong steel cylinders called bombs; in this form it is shipped to points where it is needed for water purification and for the preparation of various compounds.

**Chlorine in the World War.** Nearly all the poison gases used in the World War were either free chlorine or compounds of chlorine. Poison gas was first used by the Germans on April 22, 1915, when



a large quantity of chlorine, previously stored in cylinders hidden in the trenches, was allowed to escape. The gas, being heavy, clung to the ground and was carried forward by a favorable wind. Later in the war the use of chlorine gave way largely to certain

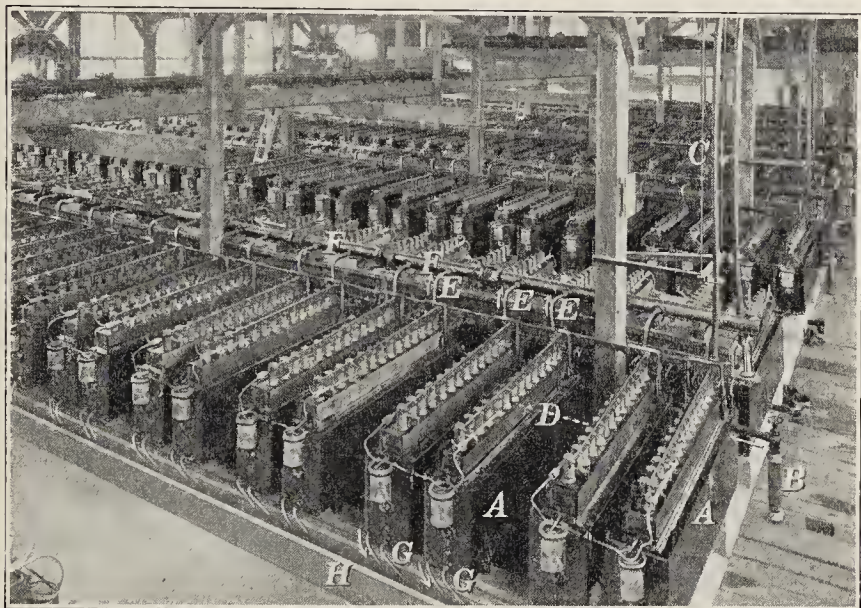


FIG. 84. View of one of the eight-cell rooms in the government chlorine plant built at Edgewood, Maryland, during the World War

This is the largest chlorine plant ever constructed, having a capacity of 100 tons of chlorine daily. The cells *A, A*, in which the sodium chloride is decomposed, are arranged side by side. A row of carbon rods *D* projects into each of the cells and constitutes the anode. A solution of salt enters the cells through the pipe *B*. The electric current enters through wires in *C* and decomposes the salt. The chlorine set free escapes from the cells through the pipes *E, E* into the larger pipe *F, F* and is then conducted to the liquefying plant, where it is liquefied and stored until desired for use. The sodium hydroxide formed flows from the cell through the pipes *G, G* into the trough *H* and is recovered by evaporating the water. For details of cell see Fig. 79

of its compounds which are more poisonous than the free element. Moreover, in place of trusting to the wind to carry the gas, the compounds were filled into shell and then fired into the ranks of the enemy. Because of the great demand for poison gas large quantities of chlorine were required. To help meet the demand the United States built, at Edgewood, Maryland, in 1917-1918, a chlorine plant with a daily capacity of one hundred tons (Fig. 84).

**Nascent state.** It will be noticed that when oxygen is set free from water by chlorine, it is *at that instant* able to do what ordinary oxygen gas cannot do, for it bleaches substances which remain unchanged in dry air or in pure oxygen. *It is generally true that the activity of an element is greatest at the instant of its liberation from its compounds.* To express this fact, elements at the instant of liberation are said to be in the *nascent state*, the word *nascent* being derived from a Latin word meaning "to be born." This greater activity is usually accounted for by supposing that an element at the instant of liberation from a compound is in the form of separate atoms and is therefore more reactive than after the atoms have combined to form molecules. When moist chlorine acts as a bleaching agent, it is nascent oxygen which does the bleaching.

**Hydrogen chloride (HCl).** Hydrogen chloride is a very important compound, since its solution in water constitutes ordinary *hydrochloric acid*, which has many commercial uses. It is a colorless gas and is 1.26 times as heavy as air. When inhaled, it has an irritating and suffocating effect. It is very soluble in water, 1 volume of water, under standard conditions, dissolving 506 volumes of hydrogen chloride. Because of this solubility the gas abstracts moisture from the air and forms minute drops of solution which constitute little clouds or fumes. At 0° it is condensed to the liquid state by a pressure of 28 atmospheres. The resulting liquid is colorless, boils at -85°, and solidifies at -111°. This liquid does not conduct electricity, has no action upon metals, and in general is very inactive.

**Laboratory preparation.** While hydrogen chloride can be prepared by burning hydrogen in chlorine (p. 179), it is much more convenient and economical to obtain it by treating common salt (sodium chloride) with sulfuric acid. Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) and hydrogen chloride are formed according to the equation:



It will be noted that in this reaction the sodium of the sodium chloride exchanges places with the hydrogen of the sulfuric acid. Such a reaction is called a *double decomposition*.

**Apparatus.** To prepare the gas the dry sodium chloride is placed in a flask *A* (Fig. 85), sulfuric acid is added through the funnel tube, and the flask is gently warmed. The hydrogen chloride is rapidly given off and can be collected by displacement of air, as in the case of chlorine (Fig. 77).

To prepare a solution of the gas the end of the delivery tube is fixed *just above* the level of some water in the cylinder *B*. The gas is very soluble and is absorbed as fast as it escapes from the tube. The sodium sulfate formed is a white solid and remains in the flask *A*.

#### Commercial preparation.

Commercially, hydrogen chloride is prepared in connection with the manufacture of sodium sulfate, the reaction being the same as that just given. It is also prepared by heating sodium hydrogen sulfate (which is obtained in the manufacture of nitric acid) with sodium chloride:



In either case the hydrogen chloride liberated is passed into water, in which it dissolves, the solution forming the *hydrochloric acid* of commerce.

**Demonstration of solubility of hydrogen chloride.** The extreme solubility of hydrogen chloride in water may be shown as follows: A perfectly dry flask *A* (Fig. 86) is filled with hydrogen chloride. This flask is connected, by means of a glass tube, with a similar flask *B* which is nearly filled with water, as shown in the figure.

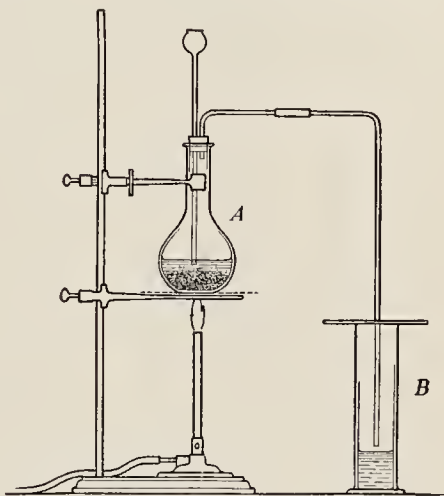


FIG. 85. The preparation of a solution of hydrogen chloride

The end of the tube opening into flask *A* is drawn out to a rather fine jet. By blowing into the tube *C*, a few drops of water are forced into *A*. Some of the hydrogen chloride at once dissolves, thus diminishing the pressure inside the flask. The water then flows continuously from *B* into *A* until nearly all the hydrogen chloride is absorbed. It is evident that the connections must be air tight.

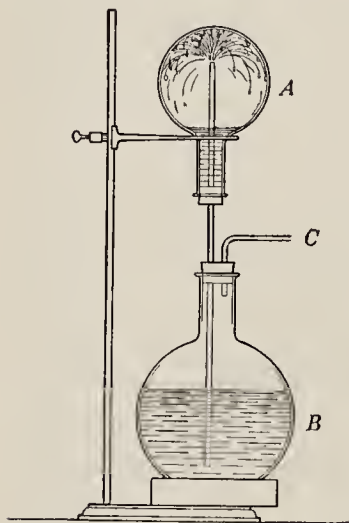
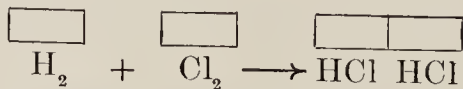


FIG. 86. Apparatus to show the extreme solubility of hydrogen chloride in water

### Composition of hydrogen chloride.

The composition of hydrogen chloride can be determined by the electrolysis of its aqueous solution. When hydrogen chloride is electrolyzed, the hydrogen of the compound is evolved at the cathode and the chlorine at the anode. A special form of apparatus is required, in order to avoid the difficulties arising from the marked solubility of the chlorine in water. When the experiment is carried out, it is found that the volume of the hydrogen liberated is exactly equal to that

of the chlorine. Conversely, it is possible to show by experiment that when hydrogen and chlorine combine, they always do so in the ratio of 1 volume of hydrogen to 1 volume of chlorine; moreover, the product is always 2 volumes of hydrogen chloride. These relations may be shown graphically in the following way:



Since chlorine is 35.18 times as heavy as hydrogen, it follows that 1 part by weight of hydrogen combines with 35.18 parts by weight of chlorine to form 36.18 parts by weight of hydrogen chloride.



**Hydrochloric acid.** Hydrochloric acid is a solution of hydrogen chloride in water. In the industries it is often called *muratic acid*. When pure materials are used in its preparation it is a colorless liquid, but the commercial acid is often colored yellow by impurities. The most concentrated solution has a density of about 1.2 and contains approximately 40 per cent by weight of hydrogen chloride. The density of its aqueous solutions increases with the amount of gas dissolved, as shown in the following table, which gives the percentage by weight of hydrogen chloride present in solutions of various densities, the measurements being taken at 15°.

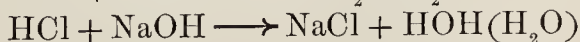
PER CENT OF HCl	DENSITY	PER CENT OF HCl	DENSITY	PER CENT OF HCl	DENSITY
5.69	1.0284	20.04	1.1006	35.02	1.1779
10.17	1.0507	25.06	1.1265	40.09	1.2013
15.22	1.0761	30.00	1.1526	43.40	1.2134

**Chemical conduct.** While hydrogen chloride has little chemical activity, its aqueous solution, hydrochloric acid, has marked properties, the most important of which are as follows:

1. **Taste.** A dilute solution of the acid has a sour taste like that of vinegar.

2. **Action on colored compounds.** It acts upon many colored compounds and changes their color in some way — very often to a red. Thus, it changes the blue color of litmus (a coloring matter obtained from a plant) to red.

3. **Action on metals and their hydroxides.** The hydroxides of the metals are compounds of a metal with hydrogen and oxygen, such as sodium hydroxide (NaOH). When hydrochloric acid is brought in contact with certain metals or with the hydroxide of the metals, the hydrogen of the acid is replaced by the metal, thus:



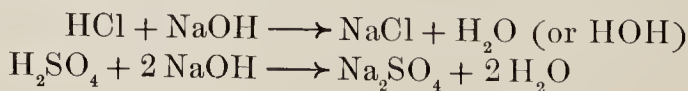


**Chlorides.** The product formed when hydrochloric acid acts upon a metal or a hydroxide is called a *chloride*. Thus, in the above reactions we obtain sodium chloride and iron chloride. With few exceptions the chlorides are solid compounds, and all except silver chloride and mercurous chloride are soluble in water. Lead chloride is soluble in hot water but not in cold.

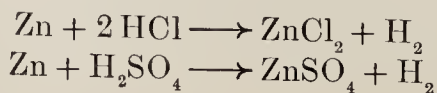
**The common acids.** It will be recalled that hydrochloric acid consists of a solution of hydrogen chloride in water. All the other common acids used so largely in the industries and in chemical laboratories are aqueous solutions of definite compounds. Thus, nitric acid is a solution of the liquid known as hydrogen nitrate, the formula of which is  $\text{HNO}_3$ ; sulfuric acid is a solution of the thick, oily liquid called hydrogen sulfate, whose formula is  $\text{H}_2\text{SO}_4$ . For most purposes it is not necessary to make a distinction between the name of the compound and its solution in water, and both are frequently called acids.

**Characteristics of acids.** A study of the acids reveals the fact that, while the individual members of the class may differ in many of their properties, they all possess certain fundamental characteristics. These characteristics are as follows:

1. All compounds forming acids in solution contain hydrogen.
2. They react with the hydroxides of metals, and in this reaction the hydrogen of the acid combines with the hydroxyl group (OH) of the base to form water. Thus, hydrochloric acid and sulfuric acid react with sodium hydroxide as indicated in the following equations:



3. As a general rule, acids act upon certain metals, dissolving the metals. In this reaction the metal displaces the hydrogen of the acid. Thus, zinc reacts with hydrochloric acid and sulfuric acid as shown in the following equations:



4. The solutions have a sour taste and change the color of certain compounds known as *indicators*. Thus, blue litmus turns red on the addition of an acid.

5. The solutions are electrolytes, and when a current of electricity is passed through them, hydrogen is usually evolved at the cathode.

**Definition of acids.** From these characteristics of acids in general we may define an acid as follows: *An acid is a compound of hydrogen whose aqueous solution (1) has a sour taste, (2) changes blue litmus to red, and (3) acts upon metals and their hydroxides, forming compounds in which the hydrogen of the acid is replaced by the metal.*

Just as the individuals composing a group of people have certain characteristics in common and yet may differ widely in certain traits, so the acids, although possessing many common properties, may differ in other properties. Thus, some are more easily decomposed than others; some are very poisonous, while others are not.

**Importance of acids.** The acids constitute one of the most important classes of compounds. A very large number are known, and we shall meet with a considerable number as we proceed. All sour fruits and vegetables owe their sourness to acids. Many physiological processes, such as digestion, depend upon them. Fats, vegetable oils, soaps, and salts of all kinds are compounds of acids with other substances. Thousands of tons of sulfuric, hydrochloric, and nitric acids are used annually in the industries.

### EXERCISES

1. Consult the dictionary for the derivation of the words *chlorine*, *acid*, *nascent*.

2. Distinguish between the words *catalysis* and *electrolysis*.

3. Contrast the properties of the elements so far studied.

4. Why not collect chlorine over water as in the case of hydrogen and oxygen?

5. In the preparation of hydrogen chloride (Fig 85), why not have the exit tube dip below the surface of the water in *B*?

6. The great center for the production of chlorine is in the vicinity of Niagara Falls. Account for the choice of this location.

7. What factors must be taken into account in selecting a location for the commercial manufacture of any chemical product?

8. Calculate the percentage composition of (a) sodium chloride; (b) hydrogen chloride.

9. What volume of chlorine can be prepared from 10 kg. of sodium chloride?

10. (a) What is the density of hydrochloric acid containing 30 per cent of hydrogen chloride? (See table, p. 187.) (b) What would 1 liter of this acid weigh? (c) What weight of hydrogen chloride would it contain? (d) What weight of sodium chloride would be necessary to prepare this weight of hydrogen chloride?

11. What volume of chlorine can be obtained by the action of 100 cc. of hydrochloric acid (density 1.1265) on manganese dioxide?

12. (a) 10 liters of chlorine will combine with how many liters of hydrogen? (b) How many liters of hydrogen chloride will be formed?

13. A certain chlorine plant produces 20 tons of chlorine daily. Calculate the weight of sodium chloride used daily, as well as the weights of the various products resulting from the electrolysis of the salt.

14. The concentrated hydrochloric acid of commerce has a density of approximately 1.20 and contains 40 per cent by weight of hydrogen chloride. What weights of raw materials are necessary for the production of 100 kg. of this acid?

15. A compound was found by analysis to have the following composition: Mn, 36.38 per cent; S, 21.23 per cent; O, 42.39 per cent. Calculate the simplest formula of the compound.

## CHAPTER XVI

### SODIUM ; SODIUM HYDROXIDE ; BASES ; NEUTRALIZATION ; SALTS ; RADICALS

**Metals and nonmetals.** The chemist finds it convenient to divide the elements into two general groups known as the *metals* and the *nonmetals*. It is the chemical conduct of an element that determines to which of these two groups it belongs. This distinction will be described more fully in a later chapter. For the present it is only necessary for us to remember that all the metals except mercury are solids, that as a rule they are good conductors of heat and electricity, and that (with the exception of gold and copper) they have a silvery luster. Most of the metals have a high density; a few, however, such as aluminum and magnesium, are comparatively light; while three (namely, lithium, sodium, and potassium) are so light that they will float on water.

The elements so far studied are all nonmetals. It is advisable now to study some one metal, and the one known as *sodium* best serves our purpose. The Latin word for sodium is *natrium*; hence the symbol Na of the element.

**Properties of sodium.** Sodium is a silver-white metal, a little lighter than water, and so soft that it can be molded easily by the fingers or pressed into wire. It melts at 97.5°. It is very active chemically, combining with most of the nonmetallic elements, such as oxygen and chlorine. It displaces hydrogen from acids. It also displaces hydrogen from water, and this reaction serves as a method for preparing hydrogen (p. 43). Because of its affinity for oxygen it tarnishes immediately on exposure to air, so that it is often kept immersed in kerosene, since it has no action upon this liquid.



**Occurrence of sodium.** Sodium does not occur in nature in a free state. The most familiar compound of the element found in nature is *sodium chloride*. This soluble compound is a constituent of all sea waters and mineral waters, and forms large, solid deposits in various parts of the world. The element also occurs as a constituent of many rocks, and its compounds are therefore present in the soil formed by their disintegration. Other compounds of sodium often found in nature are *sodium nitrate* (known commercially as *Chile saltpeter*), *sodium carbonate*, and *sodium borate*, or *borax*.

**History of sodium.** The isolation of sodium dates back to the year 1807. At that time the compounds now known as sodium hydroxide and potassium hydroxide were well known, but they were regarded as elementary in character. In 1807 Sir Humphry Davy (Fig. 76), while studying the effect of the electric current upon various substances, succeeded in decomposing these compounds and from them obtained both sodium and potassium.

**Preparation of sodium.** For many years the most economical method known for preparing sodium consisted in heating sodium carbonate (a white solid having the formula  $\text{Na}_2\text{CO}_3$ ) with carbon :



At present it is prepared by the same method which led to its discovery ; namely, by the electrolysis of its hydroxide, a white, solid compound having the formula  $\text{NaOH}$ . It is necessary to carry on the process in the absence of water, because the metal acts upon water with great vigor (p. 43). Since it is impossible to obtain the element by the electrolysis of a solution of the hydroxide, the solid compound is heated until it melts, and the current of electricity is then passed through the resulting liquid. Sodium is prepared at Niagara Falls, where water power is utilized for generating the electric current. The process is a difficult one to carry out, so that sodium is not a cheap metal.

**Commercial preparation (Castner's process).** At Niagara Falls sodium is prepared by a process devised by Castner. The sodium hydroxide is melted in a cylindrical iron vessel *A* (Fig. 87), through the bottom of which rises the cathode *B*. The anodes *C*, several in number, are suspended around the cathode from above. A cylindrical vessel *E* floats in the fused alkali, directly over the cathode, and under this cap the sodium and hydrogen liberated at the cathode collect. The hydrogen escapes by lifting the cover, and the sodium, protected from the air by the hydrogen, is from time to time skimmed or drained off. Oxygen is set free at the anode and escapes into the air through the opening *F* without coming into contact with the sodium or the hydrogen.

**Uses.** Sodium is used in preparing certain of its compounds. It is also used in making the well-known dye indigo.

**Compounds of sodium.** Sodium forms many useful compounds. One of these, *sodium hydroxide*, is a typical member of that important class

of compounds known as *bases*, and it is desirable for us to study its properties at this time; the discussion of the other compounds of sodium may well be deferred to a later chapter.

**Sodium hydroxide (caustic soda) (NaOH).** Sodium hydroxide is a brittle, white, crystalline substance which rapidly absorbs water and carbon dioxide from the air. For laboratory purposes it is ordinarily sold in the form of sticks resembling sticks of white candy. It is very soluble in water, and the solution is what is commonly used. As the name *caustic soda* indicates, it is a very corrosive substance, having a disintegrating action on most animal and vegetable tissues. It is used in a great many chemical industries, its chief uses being in the

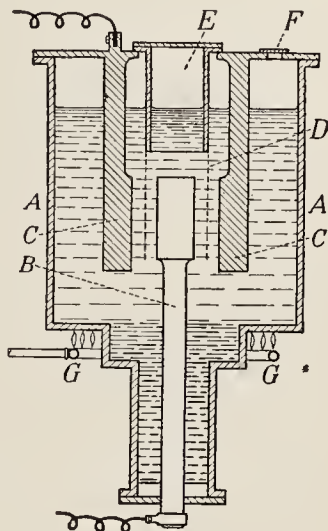
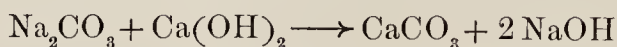


FIG. 87. A Castner cell for the electrolytic production of metallic sodium

manufacture of soap and paper and in the refining of petroleum. As a household article it is sold under the name of *lye*.

**Preparation.** Sodium hydroxide is prepared commercially by two different processes, as follows:

1. *Action of calcium hydroxide upon sodium carbonate.* This process consists in treating calcium hydroxide (slaked lime) suspended in water with sodium carbonate:



The calcium carbonate ( $\text{CaCO}_3$ ) is precipitated as a white, insoluble solid, leaving the sodium hydroxide in solution.

While this is an old process, it still remains an important one. Manufacturers of sodium carbonate often utilize a portion of their product in the preparation of the hydroxide, so that the manufacture of these two compounds is often carried on in the same plant.

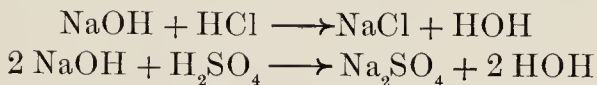
2. *Electrolytic methods.* In connection with the electrolytic preparation of chlorine (p. 177) it was stated that when an electrical current is passed through a solution of sodium chloride, both chlorine and sodium hydroxide are produced, the former escaping as a gas. Not all the sodium chloride is decomposed, so that the resulting solution contains both sodium chloride and sodium hydroxide. The chloride is much less soluble than the hydroxide, so that when the solution is partially evaporated the chloride separates, leaving a nearly pure solution of hydroxide. This is then evaporated to dryness, and the sodium hydroxide is fused to drive off all the water. As it cools, the product solidifies in the form of a white solid and in this form is sold on the market.

The product as prepared by either of the above methods is never pure. If desired, it may be further purified by treatment with alcohol, which dissolves the sodium hydroxide but only small quantities of the impurities present. Perfectly pure sodium hydroxide may best be obtained by dissolving sodium in water and evaporating the resulting solution.

**Chemical conduct.** Sodium hydroxide has certain properties in common with the hydroxides of other metals. These common properties are as follows:

1. **Action on litmus.** Its action on litmus (as well as on other colored substances) is just the opposite of that of acids; that is, it turns red litmus to a blue color.

2. **Action on acids.** It reacts with acids to form water and compounds known as *salts*, in which the hydrogen of the acid has been replaced by the metal of the base (p. 187), thus:



The compounds NaCl (sodium chloride) and Na<sub>2</sub>SO<sub>4</sub> (sodium sulfate) are typical salts.

**The common bases.** The hydroxides of the metals as a group are called *bases*. In addition to sodium hydroxide the common bases include potassium hydroxide (KOH) and calcium hydroxide (Ca(OH)<sub>2</sub>). These are white solids soluble in water. The very soluble bases with most pronounced basic properties are often called *alkalies*. While these solid compounds are often called bases, yet pronounced basic properties are exhibited only by their solutions in water.

**Characteristics of bases.** The class characteristics of the bases are as follows: (1) The compounds contain hydrogen, oxygen, and a metal. (2) When brought in contact with an acid, the metal of the base exchanges places with the hydrogen of the acid, forming water and a salt. (3) Their solutions reverse the color change produced in indicators by acids; thus, they turn red litmus blue. (4) Their solutions are conductors of electricity, and when these solutions are electrolyzed the metal is set free at the cathode.

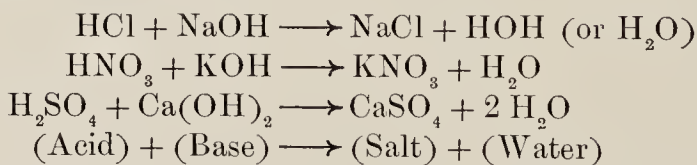
**Definition of a base.** A base may now be defined as follows:

*A base is a compound of a metal and one or more OH groups. In the presence of water (1) it changes red litmus to a blue color and (2) it reacts with an acid to form a salt and water.*



**Indicators.** We have seen that acids turn blue litmus to a red color, while bases reverse the change, turning red back to blue. We may employ litmus, therefore, to determine whether a given solution is acid or basic. It may also be used to determine whether or not a solution is *neutral* (that is, neither acid nor basic), for such solutions will have no effect on either blue or red litmus. In addition to litmus, certain other colored compounds may be used for determining whether solutions are acid, basic, or neutral; and all these are known collectively as *indicators*.

**Neutralization.** When an acid and a base are brought together in solution in the proper proportion, the characteristic properties of each disappear. It is evident, therefore, that the acid and base must have reacted with each other to form one or more new compounds which are neither acid nor basic in character. What really happens is that the hydrogen of the acid and the hydroxyl group (OH) of the base combine to form water, while the remaining constituents of the acid and base unite to form a compound which belongs to the class of compounds known as salts. These facts are shown by the following typical equations:

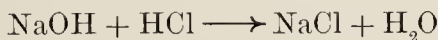


*The interaction of an acid and a base to form a salt and water is known as neutralization, and the acid and the base are said to neutralize each other.* Almost all the salts are solids. The salts formed in neutralization may usually be obtained by evaporating the water. Neutralization, therefore, serves as a general method for the preparation of salts.

**Neutralization a definite act.** If two solutions, one of a base and the other of an acid, are prepared, experiment has shown that a given volume of the acid will invariably require a perfectly definite volume of the base for its neutralization.



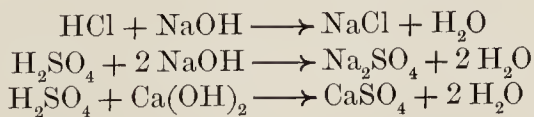
**Experimental details.** The experiment is most easily performed with the aid of burettes (Fig. 88), which are graduated tubes furnished with a stopcock at one end. The one is filled to the zero mark with the acid solution, the other with the basic. A measured volume of one solution is drawn off into a small beaker, a few drops of an appropriate indicator added, and the second solution run in with constant stirring until the indicator just turns color. If the concentration of each solution is accurately known, it is easy to calculate, from the volumes required for neutralization, the ratio by weight between the acid and base taking part in the action. Experiment shows that this ratio always bears a simple relation to that between the molecular weights of the reacting substances. Such a reaction as is indicated in the equation



is therefore perfectly definite, and if we know the weight of an acid employed, we can calculate the weight of the base required to neutralize the acid and also the weight of the salt formed.

#### Balancing equations of neutralization.

In neutralization the hydrogen of the acid combines with the hydroxyl group (OH) of the base to form water; hence, in balancing equations representing neutralization we must take the acid and the base in such proportions that the number of hydrogen atoms of the acid will be the same as the number of hydroxyl radicals of the base, thus:



**Salts.** In the discussion of acids (p. 188) and also in connection with bases (p. 195) we have learned that the hydrogen of the acid may be displaced readily by a metal. The resulting

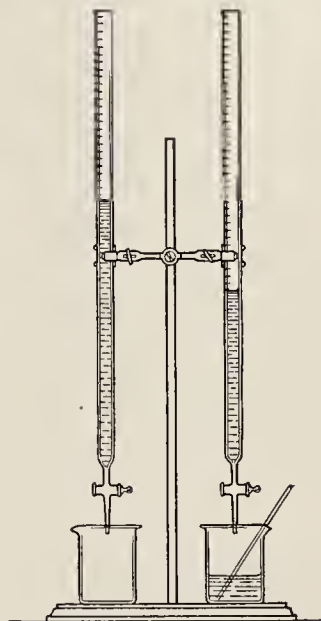
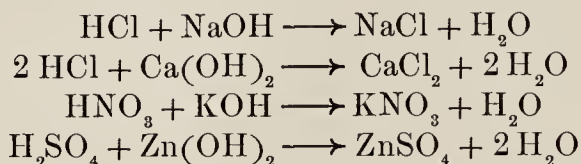


FIG. 88. Apparatus used in proving that neutralization is a definite act

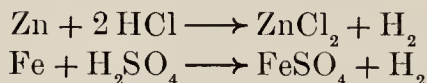
compound is known as a *salt*. *A salt may therefore be defined as a compound derived from an acid by replacing the hydrogen of the acid by a metal.*

The following equations represent the reactions taking place in the formation of some typical salts.



It is customary to speak of the salts derived from a certain acid as salts of that acid. Thus,  $\text{NaCl}$  and  $\text{CaCl}_2$  are salts of hydrochloric acid. Similarly,  $\text{KNO}_3$  is a salt of nitric acid ( $\text{HNO}_3$ ), while  $\text{ZnSO}_4$  is a salt of sulfuric acid.

Salts are also formed when a metal dissolves in an acid, as illustrated in the following equations:



In general we may expect each acid to form as many salts as there are metals, and in most cases this is what happens.

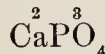
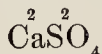
**Radicals and their valence.** If we compare the formulas  $\text{H}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{CuSO}_4$ , we shall notice that they all contain the group of atoms  $\text{SO}_4$ . Similarly, the compounds represented by the formulas  $\text{HOH}$ ,  $\text{NaOH}$ , and  $\text{KOH}$  all contain the group of atoms  $\text{OH}$ , known as the *hydroxyl* group. *Groups of atoms which act together as a unit in chemical action are called radicals.* With rare exceptions, radicals do not exist in a free state, but only in combination with other atoms or radicals. Oftentimes a molecule may contain more than one hydroxyl or other radical. Thus, calcium hydroxide contains 1 atom of calcium and 2 hydroxyl groups in each molecule. In such cases it is customary to write the formula  $\text{Ca}(\text{OH})_2$  rather than  $\text{CaO}_2\text{H}_2$ , although either is correct. Similarly, we write  $\text{Al}_2(\text{SO}_4)_3$  rather than  $\text{Al}_2\text{S}_3\text{O}_{12}$ , and  $\text{Ca}_3(\text{PO}_4)_2$  rather than  $\text{Ca}_3\text{P}_2\text{O}_8$ .

The valence of a radical can be inferred by noting the number of atoms of hydrogen (or some other univalent element) with which it combines. The radical  $\text{SO}_4$  is bivalent, for it combines with two hydrogen atoms as represented in the formula  $\text{H}_2\text{SO}_4$ . The radical  $\text{OH}$ , on the other hand, is univalent, for it combines with one atom of hydrogen to form water ( $\text{HOH}$  or  $\text{H}_2\text{O}$ ).

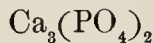
**Formulas of salts.** Knowing the valence of a metal and the formula of any acid, it is easy to deduce the formula of the salt which the metal may naturally be expected to form with the acid. Thus, suppose we wish to write the formulas of the salts which the element calcium forms with the acids  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_3\text{PO}_4$  respectively. First write the symbol of the element in place of the hydrogen of the acid:



Now write over the symbols of calcium, chlorine, and each of the radicals  $\text{SO}_4$  and  $\text{PO}_4$  the valence of each element or radical:



Finally, take such numbers of the two constituents of each salt as will add up an equal number of valences. This gives the following as the correct formulas:



**Normal salts; acid salts.** It is evident that sodium hydroxide can act upon hydrochloric acid in but one proportion:



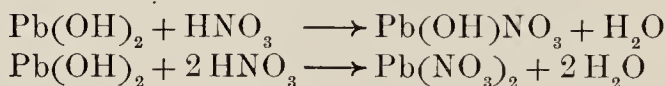
With sulfuric acid, however, the reaction may take place according to either of the following equations, depending upon the relative weights of sodium hydroxide used:



It will be observed that in the one salt ( $\text{NaHSO}_4$ ) only a portion of the hydrogen of the sulfuric acid has been displaced

by the metal, while in the other ( $\text{Na}_2\text{SO}_4$ ) all the hydrogen has been displaced. To distinguish between these two classes of salts the former is said to be an *acid salt*, while the latter is termed a *normal salt*.

**Basic salts.** When an acid such as hydrochloric acid acts upon a base such as lead hydroxide, the reaction may take place in either of the following ways:



The compound  $\text{Pb(OH)NO}_3$  is intermediate between a salt and a base; it is therefore termed a *basic salt*.

**Names of acids, bases, and salts.** Since acids, bases, and salts are so intimately related to one another, it is very advantageous to give names to the three classes in accordance with some fixed system. The system universally adopted is as follows:

**Naming of bases.** All bases are called *hydroxides*. They are distinguished from each other by prefixing the name of the element which is in combination with the hydroxyl group. Examples: sodium hydroxide ( $\text{NaOH}$ ); calcium hydroxide,  $\text{Ca(OH)}_2$ ; copper hydroxide,  $\text{Cu(OH)}_2$ .

**Naming of acids.** The method of naming acids depends upon whether the acid consists of two elements or three.

1. **Binary acids.** Acids containing only one element in addition to hydrogen are called *binary acids*. They are given names consisting of the prefix *hydro-*, the name of the second element present, and the termination *-ic*. Examples: hydrochloric acid ( $\text{HCl}$ ); hydrosulfuric acid ( $\text{H}_2\text{S}$ ).

2. **Ternary acids.** As the name signifies, ternary acids contain three elements. Hydrogen is, of course, always one of the three; and the majority of these acids also contain oxygen. In such cases it is the element other than hydrogen and oxygen that is used in naming the acid. Thus, in the acid  $\text{HNO}_3$  the element nitrogen gives its name to the acid, while in  $\text{H}_2\text{SO}_4$  it is the sulfur. It usually happens that the same three elements can

unite in different proportions to make several different acids. The most familiar one of these is given a name ending in the suffix *-ic*, while the one with less oxygen is given a similar name, but ending in the suffix *-ous*. Examples: nitric acid ( $\text{HNO}_3$ ); nitrous acid ( $\text{HNO}_2$ ). In case more than two acids are known, use is made of prefixes in addition to the two suffixes *-ic* and *-ous*. Thus, the prefix *per-* signifies an acid still richer in oxygen; the prefix *hypo-* signifies one with less oxygen. (For examples, see table below.)

**Naming of salts.** A salt derived from a binary acid is given a name consisting of the names of the two elements composing it, with the termination *ide*. Example: sodium chloride ( $\text{NaCl}$ ). All other binary compounds are named in this way.

A salt of a ternary acid is named in accordance with the acid from which it is derived. A ternary acid whose name has the termination *-ic* gives a salt with the name ending in *-ate*, while an acid with the termination *-ous* gives a salt with the name ending in *-ite*. The following table will make the application of these principles clear:

ACID	FORMULA	SALT	FORMULA
Hydrochloric . . . . .	$\text{HCl}$	Sodium chloride . . . . .	$\text{NaCl}$
Hypochlorous . . . . .	$\text{HClO}$	Sodium hypochlorite . . .	$\text{NaClO}$
Chlorous . . . . .	$\text{HClO}_2$	Sodium chlorite . . . . .	$\text{NaClO}_2$
Chloric . . . . .	$\text{HClO}_3$	Sodium chlorate . . . . .	$\text{NaClO}_3$
Perchloric . . . . .	$\text{HClO}_4$	Sodium perchlorate . . .	$\text{NaClO}_4$

### EXERCISES

1. From the method of preparation, what impurities should you expect to find in commercial sodium hydroxide?
2. Contrast the composition and properties of acids and bases.
3. Define the following terms: (1) acid, (2) base, (3) salt, (4) alkali, (5) normal salt, (6) acid salt, (7) basic salt.
4. Distinguish between atoms and radicals; between atoms and molecules.



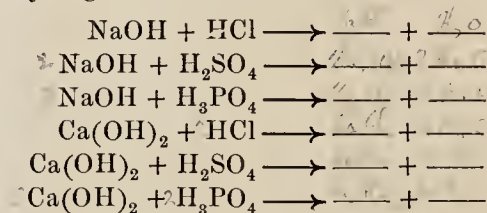
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5. What are the salts of nitric acid called? the salts of sulfuric acid?

6. Name the acids represented by the following formulas:  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$ .

7. Give the name of each of the compounds represented by the following formulas and tell to which group of compounds (acid, base, or salt) each belongs:  $\text{Mg}(\text{OH})_2$ ,  $\text{HBr}$ ,  $\text{NaBr}$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{CaSO}_3$ ,  $\text{PbSO}_4$ ,  $\text{HI}$ ,  $\text{NaNO}_2$ ,  $\text{KNO}_3$ ,  $\text{FeCl}_3$ ,  $\text{KClO}_4$ ,  $\text{Ca}(\text{ClO})_2$ ,  $\text{NaHSO}_4$ .

8. Complete and balance the following equations, assuming that in each instance the sodium or the calcium in the first compound changes place with the hydrogen of the second:



9. Write the equations for the reactions which take place when aluminium hydroxide ( $\text{Al}(\text{OH})_3$ ) is neutralized by each of the following acids:  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ . Name each of the compounds formed.

10. Sodium, calcium, and aluminum have valences of 1, 2, and 3 respectively; write the formulas of their chlorides, sulfates, and phosphates (phosphoric acid =  $\text{H}_3\text{PO}_4$ ), on the supposition that they form salts having the normal composition.

11. Iron forms one series of salts in which it has a valence of 2, and another series in which it has a valence of 3; write the formulas for the two chlorides of iron, also for the two sulfates, on the supposition that these have the normal composition.

12. What weight of sodium hydroxide is necessary for the preparation of 1 kg. of sodium?

13. When sodium acts upon water, what volume of hydrogen is liberated for each gram of sodium that reacts?

14. How many pounds of sodium chloride are necessary for the preparation of 1 ton of caustic soda?

15. Calculate the percentage composition of sodium hydroxide.

16. The government chlorine plant built during the war had a capacity of 100 tons of chlorine daily. What was the daily output of sodium hydroxide when the plant ran at full capacity?

## CHAPTER XVII

### IONIZATION AND ITS APPLICATIONS

**Introduction.** In the chapter on solutions we found that pure water does not conduct the electric current appreciably. It was pointed out, however, that when certain compounds, such as sodium chloride, sulfuric acid, and sodium hydroxide are dissolved in the water, the resulting solutions conduct the electric current more or less readily. *All those compounds whose solutions conduct the electric current are called electrolytes.* Certain other compounds, such as ordinary sugar, when dissolved in water do not conduct the electric current, and such compounds are called *nonelectrolytes*. *Experiments have shown that all electrolytes are either acids, bases, or salts.*

**Forming a theory.** It is clear that there must be something peculiar in the make-up of acids, bases, and salts that causes them, *when in solution*, to give the solution the property of electrical conductivity. We wonder whether this property is in any way connected with the fact that all acids, irrespective of their chemical compositions, have a set of properties in common (such as sour taste, the ability to turn blue litmus red, and the ability to neutralize bases), while all bases have opposite properties. The mind at once proceeds to imagine a picture of the structure of electrolytes which, if true, would agree with all these peculiarities. In other words, we form a theory of solution of electrolytes. The theory at present accepted, and strongly supported by a great accumulation of experimental evidence, is called the *theory of ionization* or, sometimes, the *theory of electrolytic dissociation*. Evidently it must be largely electrical in character to account for the facts of electrical conductivity.

## THEORY OF IONIZATION

The theory of ionization was proposed by the Swedish chemist Arrhenius in 1887. Its main points may be stated as follows:

**1. Formation of ions.** It is assumed that when certain compounds are dissolved in water their molecules fall apart, or *dissociate*, into two or more parts, called *ions*. Thus, sodium nitrate ( $\text{NaNO}_3$ ) dissociates into the ions  $\text{Na}$  and  $\text{NO}_3$ ; sodium



FIG. 89. Svante August Arrhenius  
(1859–1927)

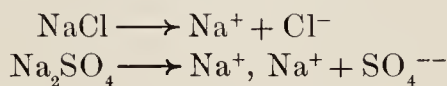
A Swedish chemist, who suggested the theory of ionization

chloride ( $\text{NaCl}$ ), into the ions  $\text{Na}$  and  $\text{Cl}$ . These ions move about in the solution independently of each other, like independent molecules, and for this reason were given the name *ion*, which means "wanderer."

**Historical.** It was Faraday who, many years earlier, suggested the name *ion* for those bodies which carry the electrical current in solutions; but he made no assumption as to their character. Arrhenius (Fig. 89) definitely assumed that they are not the same as molecules but are formed by their decomposition.

**2. The electrical charge of ions.** It is assumed that an ion differs from an atom or molecule in that it carries a large electrical charge. It is evident that the sodium ion must differ in *some* important way from ordinary sodium, for sodium ions, formed from ordinary salt, give no visible evidence of their presence in water, whereas metallic sodium at once decomposes the water. The electrical charge, therefore, greatly modifies the usual chemical properties of the element.

3. **The positive charges equal the negative charges.** It is assumed that the ions formed by the dissociation of any molecule are of two kinds: one is electrically positive, while the other is negative. The sum of all the positive charges is always equal to the sum of all the negative charges, and the solution as a whole is therefore electrically neutral. If we represent ionization by the usual chemical equations, with the electrical charges indicated by plus (+) and minus (−) signs following the symbols, the ionization of the molecules of sodium chloride and sodium sulfate is represented thus:



Those ions that are positively charged are known as *cations*, while those that are negatively charged are termed *anions*. During the process of electrolysis of a solution the cations move to the negative electrode, or cathode (p. 172), while the anions move to the positive electrode, or anode.

#### 4. Not all compounds ionize.

It is assumed that only those compounds ionize whose solutions are electrolytes. Thus, we infer that salt ionizes when dissolved in water, for it has been found that the resulting solution is a very good conductor. Sugar, on the other hand, does not ionize, for its solution is not a conductor of the electric current.

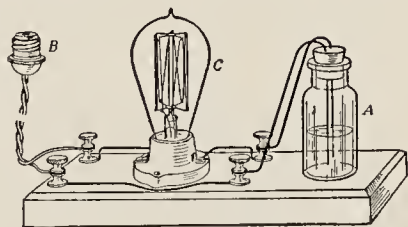
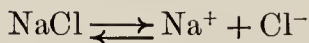


FIG. 90. A convenient form of apparatus for determining whether or not a solution is a conductor of electricity

**Laboratory apparatus.** Fig. 90 illustrates a very convenient apparatus for determining whether a solution is a good conductor. The solution is placed in the bottle *A* and the electrodes are dipped into it. Connection with the lighting circuit is made by the cord and plug *B*. If the solution is a good conductor, the current will flow through the lamp *C*, which will then glow.



5. **Extent of ionization.** It is assumed that compounds differ greatly among themselves in the ease with which they ionize in solution. Some compounds ionize readily, others only slightly, and others not at all. Again, the extent of ionization varies with the solvent. Thus, the gas known as hydrogen chloride (HCl) is largely ionized when dissolved in water, while in benzene it is not ionized at all. Water is the best ionizing solvent. Moreover, dilution aids ionization. For example, in a concentrated aqueous solution of sodium chloride only a small percentage of the molecules are ionized, an equilibrium being reached between the molecules decomposing into ions and those forming again from the ions, as expressed in the following equation :



If the solution is diluted by the addition of more water, the percentage of molecules undergoing ionization increases, and reaches a maximum only in very dilute solutions.

**Kinetic view of ionization.** To gain an adequate idea of the process of ionization it is necessary to think of it very much as we think of gases in connection with the kinetic theory (p. 64). The molecules of both solvent and solute are in active motion and are in constant collision with each other. At times these collisions result in the separation of some molecules of the electrolyte into ions. At other times ions of opposite charges meet and once more unite into molecules. The *extent* of ionization is merely the *average resultant* of these two processes. Some electrolytes are more easily knocked or pulled apart into ions than others, and their percentage of ionization at any one time is therefore greater. If we dilute the solution, we separate the existing ions more widely and diminish their chances of meeting and uniting, whereas the process of ionization goes steadily on. The *percentage* of ionization is therefore increased by dilution.

**Nature of electrical charges.** It is now quite certain that an atom is a complex system much like a miniature solar system. Nearly all the mass of the atom is in a central nucleus



consisting of positive units, each having the mass of a helium atom or possibly of a hydrogen atom. Each neutral atom also contains negative charges equal in number to the positive charges of the nucleus. These negative charges consist of electrical atoms called *electrons*, which are about  $\frac{1}{1845}$  of the weight of a hydrogen atom. Some of these electrons form a part of the nucleus, binding together the heavier positive charges; the remainder are outside the nucleus and move about it somewhat like the satellites about a planet. (A more complete discussion of the structure of the atoms is given in the chapter dealing with the periodic law.)

Under certain conditions one or more of these satellite electrons can be detached from metallic atoms, leaving the atom with one or more excess positive charges. Nonmetallic atoms may capture one or more electrons from other atoms and so become negatively charged. An electrical battery or dynamo is a machine that detaches electrons from the metal conductors and drives them around the circuit. Electrical energy is the energy of these moving electrons.

**Source of the charge upon the ions.** Applying these views to the electrification of ions, we assume that before union the atoms of sodium and chlorine have each their normal number of electrons. When these combine to form sodium chloride, one satellite electron of the sodium atom becomes shared by the chlorine atom, and the hold of the chlorine atom on it appears to be stronger than that of the sodium atom. When the molecule of sodium chloride is dissolved in water, it is easily dissociated, but the sodium loses its electron to the chlorine. The sodium atom is now positively charged; the chlorine, negatively. Upon recombination the original condition of the two atoms is restored, and the molecule is electrically neutral. The ions are therefore very different things from the atoms; they should even have different weights, though we cannot verify this experimentally.

## APPLICATIONS OF THE THEORY OF IONIZATION

In order to be of value the theory of ionization must be in accord with the chief properties of solutions. Let us now see how well the theory corresponds with the known facts.

1. **The theory of ionization and the boiling and freezing points of solutions.** We have seen that the boiling point of a liquid is raised in proportion to the number of molecules of a solute dissolved in the liquid. It has been found that *in the case of electrolytes* the boiling point is raised *more* than it should be to conform to this law. If the solute dissociates into ions, the reason for this becomes clear. *Each ion has the same effect on the boiling point that a molecule has*, and since their number is always greater than that of the molecules from which they were formed, the effect on the boiling point is abnormally great.

In a similar way the theory furnishes an explanation of the abnormal lowering of the freezing point of electrolytes, the lowering of the vapor pressure, and the increase of osmotic pressure.

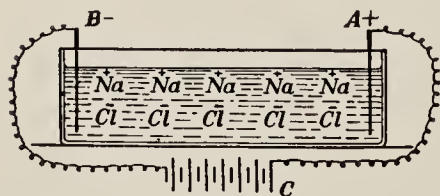


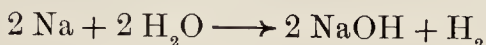
FIG. 91. Diagram illustrating the theory of the electrolysis of sodium chloride (NaCl)

2. **The theory of ionization and electrolysis.** The changes taking place during electrolysis harmonize very completely with the theory of ionization. This will be-

come clear from a study of the following examples:

**a. Electrolysis of sodium chloride.** Fig. 91 represents a vessel in which the electrolyte is a solution of sodium chloride (NaCl). According to the theory of ionization the molecules of sodium chloride dissociate into the ions  $\text{Na}^+$  and  $\text{Cl}^-$  as soon as the compound dissolves in water. Since the cathode *B* has a large negative charge derived from the battery *C*, the  $\text{Na}^+$  ions are attracted to it. On coming in contact with the cathode they

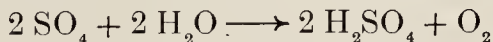
give up their positive charge and are then ordinary sodium atoms. They immediately decompose the water according to the equation



In a similar way the chlorine ions ( $\text{Cl}^-$ ) are attracted to the positively charged anode *A*, and upon giving up their charge to it they are set free as chlorine atoms. These atoms combine with each other to form molecules of chlorine gas, which is evolved at the anode (a small percentage of the chlorine reacts with the water (p. 180)).

*It is to be carefully noted that the current does not bring about the decomposition of the solute into ions; also that the current can pass through the solution only when ions are already present.* This is in complete accord with the experimental fact that no work is done by the current in decomposing the electrolyte. Consequently the current does not produce the ions.

**b. Electrolysis of water.** The reason for the addition of sulfuric acid to water in the preparation of oxygen and hydrogen by electrolysis (p. 19) can now be made clear. Water itself is not an electrolyte to an appreciable extent, for it does not form enough ions to carry a current. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) dissolved in water is an electrolyte, and dissociates into the ions  $2 \text{H}^+$  and  $\text{SO}_4^{--}$ , each  $\text{SO}_4^{--}$  ion having two negative charges. In the process of electrolysis of the solution the  $\text{H}^+$  ions travel to the cathode and, on being discharged, escape as hydrogen gas. The  $\text{SO}_4^{--}$  ions, when discharged at the anode, act upon the water, setting free oxygen and once more forming sulfuric acid:

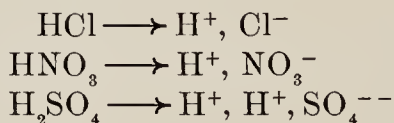


The sulfuric acid so formed at once ionizes, and the process repeats itself as long as any water is left. Hence the hydrogen set free in the electrolysis of water really comes *directly* from the acid but *indirectly* from the water; the oxygen, on the other hand, comes directly from the water.

**Properties of electrolytes dependent upon the ions present.** When a compound capable of forming ions is dissolved in water, the properties of the solution will depend upon two factors: (1) the ions formed from the compound; (2) the undissociated molecules. Since the ions are usually more active chemically than the molecules, most of the chemical properties of an electrolyte are due to the ions rather than to the molecules.

The solutions of any two compounds which give the same ion will have certain properties in common. Thus, all solutions containing the copper ion  $\text{Cu}^{++}$  are blue, unless the color is modified by the presence of ions or molecules having some other color; aqueous solutions of all chlorides give a precipitate with silver nitrate, since all such solutions contain the chlorine ion  $\text{Cl}^-$ .

**3. The theory of ionization and acids.** In water as a solvent all acids are electrolytes and are therefore ionized. The ionization takes place in such a way as to form hydrogen cations ( $\text{H}^+$ ), while the remainder of the molecule constitutes the anion. These relations are indicated in the equations

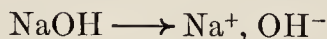


It will be noted that the one constituent common to all acids is the hydrogen ion,  $\text{H}^+$ . Accordingly the properties which all these acids have in common, such as their sour taste, their effect upon blue litmus, and their action on metals and their hydroxides, must be due to the hydrogen ions. From the standpoint of the ionization theory, therefore, *we may define an acid as a solution containing hydrogen ions.*

**Undissociated acids.** When compounds whose aqueous solutions form acids are perfectly free from water, they have no real acid properties. Neither do they have acid properties when they are dissolved in liquids, like benzene, which do not have

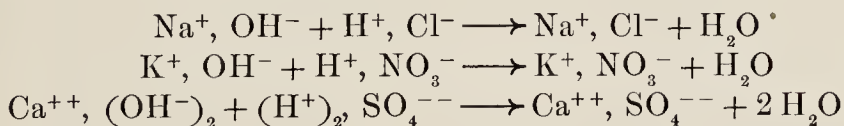
the power of dissociating them into ions. For example, a benzene solution of hydrogen chloride has no action on litmus.

4. **The theory of ionization and bases.** When dissolved in water, the molecules of the base dissociate into two kinds of ions. One of these is always composed of the group (OH) and is the anion. It is called the *hydroxyl* ion. The remainder of the molecule, which usually consists of a single atom, is the cation; thus,

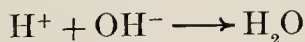


Since all bases produce hydroxyl anions, while the cations of each are different, the properties which all bases have in common when in solution must be due to the hydroxyl ions. From the standpoint of the ionization theory, therefore, *we may define a base as a solution that contains hydroxyl ions.*

5. **The theory of ionization and neutralization.** Since both acids and bases are ionized in solution, neutralization must be regarded as a reaction taking place *between ions*. We may therefore write the equation for the reaction between a base and an acid in the following form:



Experiment shows that pure water will not conduct the electric current except to a very slight extent, and therefore itself ionizes very little. Consequently, when the hydrogen ions ( $\text{H}^+$ ) of an acid and the hydroxyl ions ( $\text{OH}^-$ ) of a base meet in solution, they combine to form water and do not again part into ions. The other ions present take no part in the reaction. The essential reaction of neutralization is therefore as follows:

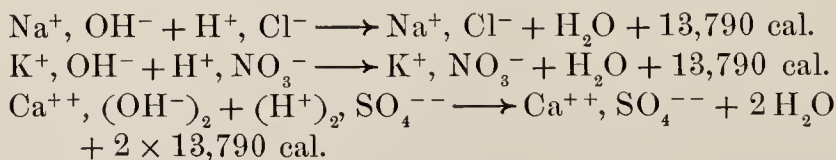


From this standpoint *we may therefore define neutralization as the union of the hydrogen ion of an acid with the hydroxyl ion of a base to form water.*

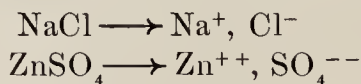


6. **The theory of ionization and salts.** It will be observed that in neutralization the cation of the base and the anion of the acid are not changed but remain as ions in the solution. If now the water present is expelled by evaporation, the two ions unite to form a compound which, with few exceptions, is a solid and remains as a residue in the dish. Thus, the ions  $\text{Na}^+$  and  $\text{Cl}^-$  unite to form the white solid  $\text{NaCl}$ ; similarly, the ions  $\text{K}^+$  and  $\text{NO}_3^-$  unite to form potassium nitrate ( $\text{KNO}_3$ ), while the ions  $\text{Ca}^{++}$  and  $\text{SO}_4^{--}$  unite to form calcium sulfate ( $\text{CaSO}_4$ ). From the standpoint of the theory of ionization *we may therefore define a salt as a compound formed by the union of the cation of a base with the anion of an acid.*

**Heat of neutralization.** If neutralization is due solely to the union of hydrogen ions with hydroxyl ions, it follows that when a given weight of water is formed in neutralization, the heat set free should always be the same, no matter from what acid and base the two kinds of ions have been supplied. Careful experiments have shown that this is the case, provided no other reactions take place at the same time. When one gram-molecule (18 g.) of water is formed in neutralization, 13,790 cal. of heat is set free. This is represented in the equations



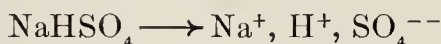
**Ionization of salts.** All salts that dissolve in water ionize in solution, the metal of the salt forming the cation, while the rest of the molecule forms the anion, as shown in the following equations:



It will be seen that salts differ from acids and bases in that the solutions have no common ion. It follows that salts do not have so many common characteristics as do acids and bases.

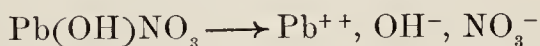
**Ionization of acid salts and of basic salts.** We have seen that an acid containing more than one replaceable hydrogen atom, such as the acid  $\text{H}_2\text{SO}_4$ , may have only one replaced by a metal forming an *acid salt* (p. 199). Thus, sodium hydrogen sulfate has the formula  $\text{NaHSO}_4$ .

Acid salts, when dissolved in water, give hydrogen ions in addition to the ions characteristic of salts; thus,



They have, therefore, the properties of an acid as well as those of a salt.

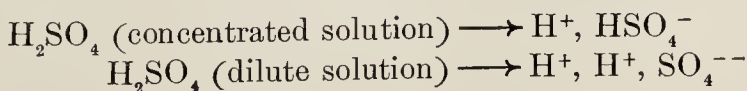
On the other hand, a base with two hydroxyl groups, such as  $\text{Pb}(\text{OH})_2$ , may have one hydroxyl group replaced by an acid radical while retaining the other. The resulting compound is a *basic salt* (p. 200), of which basic lead nitrate ( $\text{Pb}(\text{OH})\text{NO}_3$ ) is an example. When dissolved in water, a basic salt gives hydroxyl ions, characteristic of bases, in addition to the ions characteristic of a salt; thus,



Basic salts, therefore, have the properties of a base as well as those of a salt.

**Extent of ionization.** A number of factors influence the extent of ionization (p. 206), and two of these are of the greatest importance.

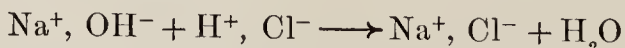
**1. The concentration of the solution.** In concentrated solutions only a very small percentage of the molecules ionize. As the solution is diluted the percentage increases, and in dilute solutions it may be very large, though it is never complete in any ordinary solution. Moreover, an acid such as sulfuric acid may form different ions according to the concentration of the solution:



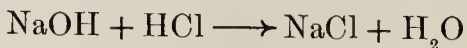
2. *The nature of the dissolved compound.* At equal concentrations, substances differ much among themselves in percentage of ionization. Most salts are about equally ionized. Acids and bases, on the contrary, show great differences.

**Strength of acids and bases.** Since acid and basic properties are due to hydrogen ions and hydroxyl ions respectively, the acid or base which will produce the greatest percentage of these ions at a given concentration must be regarded as the strongest representative of its class. To say that the *hydrogen ion concentration* of a solution is very great is therefore equivalent to saying that the solution has strongly acid properties. The acids and bases described in the foregoing paragraphs are all quite strong. In 10 per cent solutions about half the molecules are dissociated into ions, and this is also approximately the extent to which most salts are ionized at this same concentration. Many other acids, some of which we shall study later, dissociate only to a slight extent and hence are weak acids.

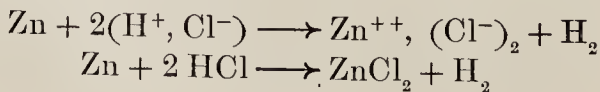
**Methods of expressing reactions between compounds in solution.** Chemical equations representing reactions between compounds in solution may represent the details of the reaction, or they may simply indicate the final products formed. Thus, if we wish to call attention to the details of the reaction between sodium hydroxide and hydrochloric acid in solution, representing the ions which take part in the reaction, we write the equation as follows:



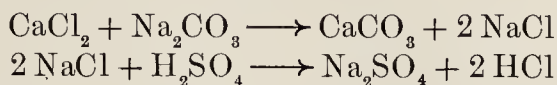
If we wish simply to represent the substances taking part in the reaction and the final products formed, we write the equation thus:



Similarly, the two ways of expressing the reaction between zinc and hydrochloric acid are



**Double decomposition.** The great majority of the reactions which we shall study are ones in which the two metals of two salts change places, or the hydrogen of an acid changes places with the metal of a salt; thus,



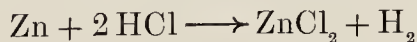
Such reactions are called *double decomposition*, and chemists have long been puzzled by the ease and rapidity with which such reactions take place.

If all salts and strong acids are largely ionized in solution, and the ions are in an active state and free to combine, we can understand why such reactions should be so nearly instantaneous when two solutions are mixed.

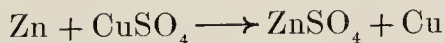
**Thermoneutrality.** When double decomposition takes place in solution, very little heat is either absorbed or evolved, and this is known as the *law of thermoneutrality*. Chemists have long wondered at this fact, because reactions of all other kinds that go on rapidly of their own accord always evolve much heat.

If electrolytes are largely ionized in solution and ions unite and part very easily, we can see why double decomposition produces so much less heat than reactions of other kinds.

**Electrochemical series.** Upon bringing a piece of zinc into a solution of an acid, zinc passes into solution and hydrogen is evolved:



In like manner, when zinc is placed in a solution of a salt of copper, such as the sulfate  $\text{CuSO}_4$ , zinc passes into solution, and a corresponding quantity of copper is precipitated:



On the other hand, copper has no effect upon a solution of zinc sulfate.

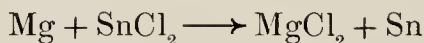
It has been found to be possible to arrange hydrogen and the metals in a table in such a way that any element in the

list will displace any one below it from its salts and will in turn be displaced from its salts by any one above it. This list is called the *electrochemical series* or the *displacement series*.

## ELECTROCHEMICAL SERIES OF THE METALS

1. Cesium	8. Aluminum	15. Nickel	22. Antimony
2. Rubidium	9. Manganese	16. Tin	23. Mercury
3. Potassium	10. Zinc	17. Lead	24. Silver
4. Sodium	11. Chromium	18. <i>Hydrogen</i>	25. Palladium
5. Lithium	12. Cadmium	19. Copper	26. Platinum
6. Calcium	13. Iron	20. Arsenic	27. Gold
7. Magnesium	14. Cobalt	21. Bismuth	28. Osmium

This table enables us to foretell many reactions. For example, from the positions of the two metals we should expect magnesium to displace tin from its salts:



We should not, however, expect iron to displace aluminum.

It is of especial interest to notice the position of hydrogen in the series. All the metals above it will evolve hydrogen from acids, while those below it will not. In the latter case, if any action takes place it must be preceded by oxidation.

**Explanation of electrochemical series.** From the standpoint of modern electrical theory this list really represents the relative ease with which the various atoms give up one or more electrons to form ions. Cesium, the metal going into solution most readily, parts with an electron most easily, while such metals as gold and platinum retain their normal number of electrons most tenaciously.

## EXERCISES

1. Suggest an explanation for the fact that solutions of certain salts sometimes change in color upon dilution.

2. From the standpoint of the ionization theory write the equation for the reaction that takes place when sodium hydroxide and sulfuric acid neutralize each other.



3. What is the action of sodium upon water? How do you account for the fact that the sodium ions present in a solution of sodium chloride do not decompose the water?

4. The  $\text{SO}_4$  ion always bears a double charge of electricity as represented by the expression  $\text{SO}_4^{--}$ . What action occurs when this ion gives up its charge of electricity, as in the electrolysis of dilute sulfuric acid?

5. What changes should you expect to take place if a current of electricity were passed through an aqueous solution of copper sulfate ( $\text{CuSO}_4$ )? Illustrate by diagram similar to Fig. 91.

6. Contrast the effects in composition produced by adding water to concentrated solutions of sugar and salt respectively.

7. When perfectly dry sulfuric acid (hydrogen sulfate) is treated with perfectly dry sodium hydroxide, no chemical change takes place. Explain.

8. When cold concentrated sulfuric acid is added to zinc, no change takes place. Recall the action of dilute sulfuric acid on the same metal. How do you account for the difference?

9. A solution of hydrogen chloride in benzene does not conduct the electric current. When this solution is treated with zinc, will hydrogen be evolved? Explain.

10. (a) Write equation for preparation of hydrogen from zinc and dilute sulfuric acid. (b) Rewrite the same equation from the standpoint of the theory of electrolytic dissociation. (c) Subtract the common ion ( $\text{SO}_4$ ) from both members of the equation. (d) From the resulting equation, explain in what the preparation of hydrogen consists when examined from the standpoint of this theory.

11. In the same manner as in the preceding exercise explain in what the action of sodium on water to produce hydrogen consists.

12. What reaction should you expect to take place when a strip of iron is placed in a solution of ferrous sulfate ( $\text{FeSO}_4$ )?

13. Which of the following metals should you expect to liberate hydrogen from dilute sulfuric acid: (a) zinc; (b) copper; (c) magnesium; (d) mercury; (e) sodium?

## CHAPTER XVIII

### COMPOUNDS OF NITROGEN

**Introduction.** Among the common elements nitrogen occupies a unique position. Vast quantities of it occur as nitrogen gas in the atmosphere, but very little of it is found as a constituent of the mineral part of the earth's crust. The chief minerals containing it are Chile saltpeter ( $\text{NaNO}_3$ ) and various grades of soft coal and shale. Very small quantities of nitrogen compounds are, however, present in all fertile soils, and these are absolutely essential to all living organisms. The plants absorb the nitrogen compounds from the soil, and the animals obtain their supply from the plants. In both plants and animals the compounds of nitrogen are built up into the form of proteid matter, which consists of carbon, oxygen, hydrogen, nitrogen, and often phosphorus and sulfur.

**Nitrogen compounds unstable.** Nearly all the compounds of nitrogen are unstable and tend to go to pieces in various ways, with the result that nitrogen is once more set free as nitrogen gas and is returned to the atmosphere. For this reason nearly all the high explosives are compounds of nitrogen. Apparently the nitrogen molecule  $\text{N}_2$  is the most stable form of nitrogen (approaching the rare gases of the atmosphere in this respect), and the atoms of nitrogen in various compounds tend to leave these compounds and form the stable nitrogen molecule. Since nitrogen compounds are essential to soil fertility, one great industrial problem is to get the free nitrogen of the atmosphere returned to the soil in the form of compounds available for plant growth.

A great many compounds of nitrogen have been prepared, but we shall consider only a few of the simplest ones, especially those with hydrogen or with oxygen.

### COMPOUNDS OF NITROGEN WITH HYDROGEN

Nitrogen forms three simple compounds with hydrogen, the names and formulas of which are as follows: ammonia ( $\text{NH}_3$ ), hydrazine ( $\text{N}_2\text{H}_4$ ), and hydronitric acid ( $\text{HN}_3$ ). Of these ammonia is by far the most important.

**Ammonia.** Ammonia is a colorless gas having a strong, suffocating odor. Under standard conditions 1 liter of the pure gas weighs 0.7708 g., being 0.59 times as heavy as air. The gas is easily condensed to a colorless liquid boiling at  $-33.3^\circ$ , and in this form is an article of commerce. Liquid ammonia, like water, is not only an excellent solvent but also a highly ionizing one. Ammonia can be obtained in the form of a snowlike solid melting at  $-77.7^\circ$ .

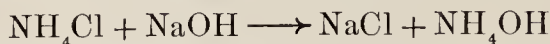
Ammonia is extremely soluble in water; at 760 mm. pressure 1 liter of water dissolves 1298 liters of the gas at  $0^\circ$ , and 710 liters at  $20^\circ$ . In dissolving such large volumes of the gas the water expands considerably, so that the density of the solution is less than that of water. The most concentrated commercial solutions have a density of 0.88 and contain 35.6 per cent by weight of the gas. The density and composition of some other strengths of solutions are shown in the following table:

Density . . . .	1.00	0.990	0.980	0.970	0.950	0.930	0.910	0.890	0.880
Per cent of $\text{NH}_3$ by weight . .	0.00	2.31	4.80	7.31	12.74	18.64	24.99	31.73	35.60

**Preparation of ammonia.** The principal methods for preparing ammonia are as follows:

1. **Laboratory method.** In the laboratory, ammonia is usually prepared from ammonium chloride ( $\text{NH}_4\text{Cl}$ ), a white solid obtained in the manufacture of coal gas. When a mixture

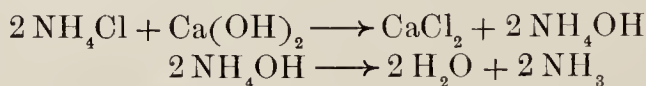
of ammonium chloride and sodium hydroxide is heated, the ammonium radical ( $\text{NH}_4$ ) and the sodium atom change places, as represented in the following equation:



The resulting ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) is unstable and, as fast as it is formed, breaks down into water and ammonia:



Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) is frequently used in place of the more expensive sodium hydroxide:



**Laboratory apparatus.** The ammonium chloride and calcium hydroxide are mixed and placed in a flask *A*, arranged as in Fig. 92.

The mixture is gently warmed, when ammonia is evolved as a gas and, being much lighter than air, is collected in *B* by displacement of air, as shown in the diagram.

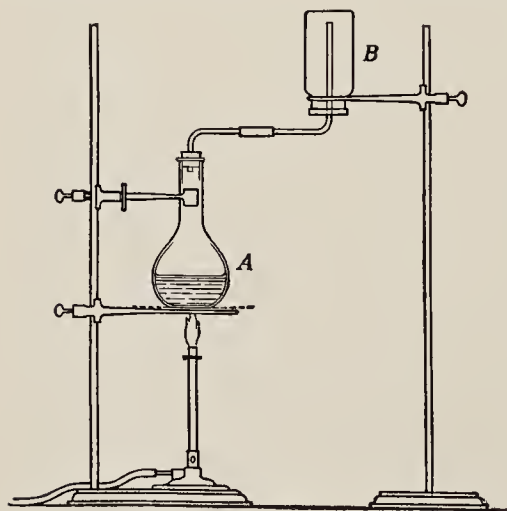
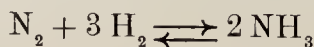


FIG. 92. Diagram of apparatus used in the preparation and collection of ammonia in the laboratory

**2. The synthetic method (Haber process).** When a mixture of hydrogen and nitrogen is heated, or subjected to the action of an electrical discharge, a small percentage of ammonia is formed. The small yield is due to the fact that some of the

ammonia formed is decomposed, and a balance, or equilibrium, between these two actions is reached, which may be expressed as follows:



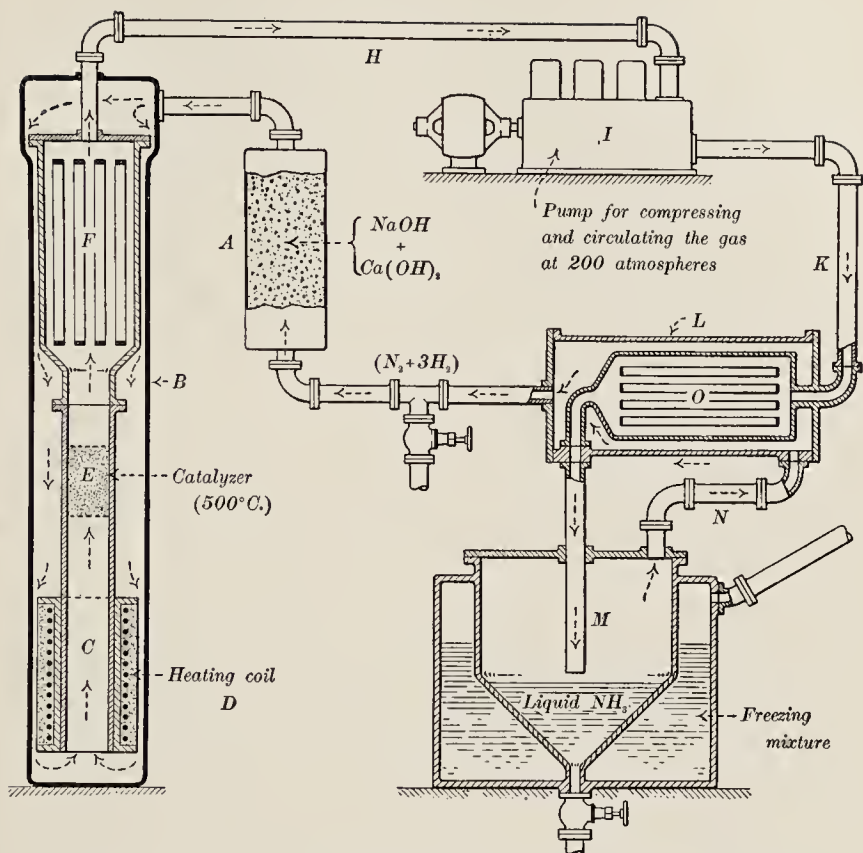


FIG. 93. Diagram illustrating the principle of the Haber process

The mixture of nitrogen and hydrogen is dried by passing it through container *A*. The dried gases then pass on, as indicated by the arrows, down to the bottom of container *B* and up through tube *C*. The gases, heated by the heating coil *D*, as indicated in the figure, pass through the catalyzer *E*, where the combination of the two gases takes place. The resulting mixture of ammonia, nitrogen, and hydrogen passes upward through the tubes *F* and is cooled somewhat by the current of nitrogen and hydrogen passing down the container *B*. The mixture flows on through *H*, as indicated by the arrows, and down into the container *L*, where it is still further cooled by passing over the tubes *O*. It then passes into the container *M*, which is kept cooled by a freezing mixture. Here the ammonia separates in liquid form while the uncombined nitrogen and hydrogen pass upward through *N* into *L* and back again into the drying tube *A*. Additional quantities of nitrogen and hydrogen are constantly added to take the place of those withdrawn in the formation of ammonia.



The best yields have been obtained by a method devised by the German chemist Haber and the French chemist Le Rossignol. This method (Fig. 93) consists in heating a mixture of nitrogen and hydrogen under a pressure of 200 atmospheres to a temperature of about  $500^{\circ}$ , in contact with a catalyzer made up of iron mixed with small quantities of a compound of potassium and aluminum. Under these conditions about 8 per cent of the nitrogen combines with the hydrogen. The ammonia thus formed is removed by cooling the resulting mixture to a point at which the ammonia liquefies, or by treatment with water or dilute acids.

**3. Commercial preparation.** In the United States nearly all the ammonia used commercially is obtained as a by-product in the process of manufacturing coal gas and coke. Certain grades of soft coal are best adapted to this purpose. Such coal contains, in addition to carbon, about 1 per cent of nitrogen and 7 per cent of hydrogen, as well as small percentages of other elements. When such coal is heated in retorts from which the air is excluded (p. 135), complicated changes take place, resulting not only in the formation of the combustible gases which constitute coal gas, but also of ammonia and many other valuable products. From 25 to 50 per cent of the nitrogen present in the coal is converted into ammonia. The volatile matter expelled from the coal is passed through water, which absorbs the ammonia, together with certain other compounds, forming a solution known as the *ammoniacal liquor*. When this liquor is heated with slaked lime, ammonia is evolved and is absorbed either in water or in a dilute solution of an acid. A very limited amount of ammonia is obtained commercially by the action of steam on the compound known as cyanamide, as will be explained in a later chapter.

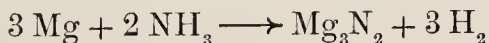
In Germany the Haber process is the chief source of ammonia. The nitrogen used in its preparation is obtained from the atmosphere, and the hydrogen from water. This method is coming into use to some extent in the United States. In order to develop it here, and to study the various problems connected with the manufacture of ammonia from atmospheric nitrogen, the United States has established, near Washington, D.C., the Fixed Nitrogen Research Laboratory, where extensive researches are being conducted.

In the Haber process a yield of 8 per cent of ammonia is obtained. If practical methods could be found for bringing about the combination at a lower temperature or at higher pressure (or both), the yield would be correspondingly increased. In the Claude modification of the Haber process now coming into use a pressure of 900 atmospheres is used, and the yield is increased to 40 per cent.

**Historical.** Inasmuch as ammonia is formed in certain natural processes which are constantly taking place about us, such as the decay of nitrogenous organic matter, it is easy to understand why this compound has been known for so long a time. It was originally prepared by heating such tissues as the hoofs and horns of animals, and the aqueous solution of the gas so obtained was termed *spirits of hartshorn*. The pure gas itself was first prepared by Priestley in 1774, and its composition was determined soon after by the French chemist Berthollet.

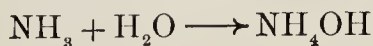
**Chemical conduct.** At ordinary temperatures ammonia is a stable compound. When heated to high temperatures, however, or when subjected to the action of an electric discharge, it is decomposed into its elements. It will burn in an atmosphere of oxygen, but not in air unless heat is continuously applied.

The hydrogen of ammonia can be displaced by metals by passing the gas over the heated metal, forming *nitrides*. Thus, magnesium forms the white solid magnesium nitride ( $\text{Mg}_3\text{N}_2$ ):

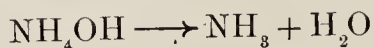


It will be observed that the decomposition of ammonia by heating is just the reverse of the formation of ammonia in the Haber process. These reactions will be discussed in Chapter XIX.

**Ammonium hydroxide ( $\text{NH}_4\text{OH}$ ).** The solution of ammonia in water, commonly called *aqua ammonia* or *ammonia water*, has strong basic properties. It turns red litmus blue and neutralizes acids, forming salts with them. It seems certain, therefore, that *when ammonia dissolves in water it combines chemically with the water* according to the equation



The resulting compound,  $\text{NH}_4\text{OH}$ , is called *ammonium hydroxide* and is a base, just as sodium hydroxide is a base. The separation of the pure hydroxide from its solutions has not been accomplished, for as the solution becomes concentrated the compound decomposes again into ammonia and water:

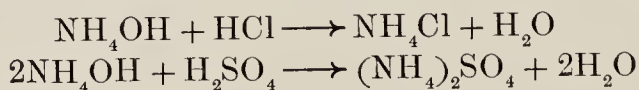


The solution of ammonia in water, therefore, constitutes a state of equilibrium between ammonia and water, on the one hand, and ammonium hydroxide, on the other. The ammonium hydroxide in turn ionizes and so is in equilibrium with the ions  $\text{NH}_4^+$  and  $\text{OH}^-$ . This condition is conveniently expressed in the following way:



Aqua ammonia is a good solvent for grease and is a familiar household article.

**Ammonium salts.** When an acid is added to aqua ammonia, the ammonium hydroxide and the acid neutralize each other according to the following equations:

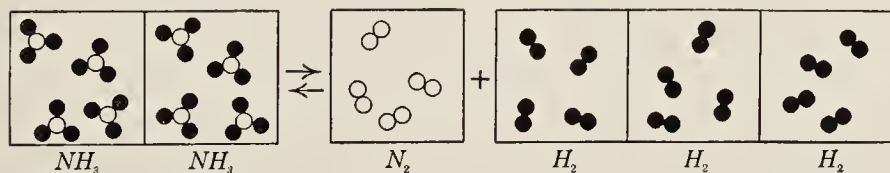


Upon evaporation the resulting salts,  $\text{NH}_4\text{Cl}$  and  $(\text{NH}_4)_2\text{SO}_4$ , are obtained in the form of white solids. In these salts the radical  $\text{NH}_4$  plays the part of a metal. On this account the name *ammonium* is given to it, since the names of most of the metals end in *ium*. Salts containing this radical are known as *ammonium salts*. Some of the most common of these salts are ammonium chloride ( $\text{NH}_4\text{Cl}$ ), ammonium sulfate  $((\text{NH}_4)_2\text{SO}_4)$ , and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ).

**Uses of ammonia.** Large quantities of ammonia are used in the manufacture of aqua ammonia, as well as in the formation of ammonium compounds, such as ammonium chloride and ammonium sulfate. In the liquid state it is also used

extensively in the manufacture of artificial ice (p. 127). Its use for this purpose is based on the facts that the gas is easily liquefied by pressure and that the resulting liquid has a relatively high heat of vaporization.

**Composition of ammonia.** That ammonia is a compound of nitrogen and hydrogen is proved by the fact that it may be formed by the direct union of the two elements (see method of preparation). The quantitative composition of the compound may be determined by taking advantage of certain reactions which make it possible to liberate the nitrogen as well as the hydrogen from any definite volume of ammonia. By measuring the volumes of the gases so liberated one can compare them not only with each other but also with the volume of the ammonia from which they were derived. In this way it has been proved that 2 volumes of ammonia yield on decomposition 1 volume of nitrogen and 3 volumes of hydrogen, as expressed graphically in the following equation, in which the atoms of hydrogen and the atoms of nitrogen are represented respectively by black and white circles:



Conversely, 1 volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia.

**Hydrazine ( $N_2H_4$ ).** This is a colorless liquid boiling at  $113.5^\circ$ . Like ammonia, it combines with water to form a base, from which salts can be prepared by the action of acids.

**Hydronitric acid ( $HN_3$ ).** This acid is a colorless liquid of disagreeable odor. It boils at  $37^\circ$  and is violently explosive.

**Law of combining volumes.** It is a very striking fact that the volumes of nitrogen and of hydrogen that combine to form ammonia, as well as that of the ammonia formed, can be



expressed *exactly* by the simple integer ratio 1 : 3 : 2. It will be recalled that in the formation of steam the ratio by volume is exactly 2 volumes of hydrogen + 1 volume of oxygen forms 2 volumes of steam (p. 79). Also, 1 volume of hydrogen + 1 volume of chlorine forms 2 volumes of hydrogen chloride. More than a century ago the French chemist Gay-Lussac investigated many cases of this kind and reached a general conclusion known as *the law of combining volumes* or *the law of Gay-Lussac*. This law may be stated thus: *When two gases combine, there is an integer ratio between their volumes as well as between the volume of either one of them and that of the product, provided it is a gas.* The principle of Avogadro affords a ready explanation of this striking law, and it was the law of combining volumes that led Avogadro to advocate his famous principles.

## COMPOUNDS OF NITROGEN WITH HYDROGEN AND OXYGEN

Nitrogen forms a number of compounds with hydrogen and oxygen, the most important of which are the two acids, nitric acid ( $\text{HNO}_3$ ) and nitrous acid ( $\text{HNO}_2$ ).

Because of its great activity nitric acid does not occur free in nature, but a number of its salts are found in considerable quantities. The most abundant of these is sodium nitrate ( $\text{NaNO}_3$ ), which is found in large quantities in Chile and is known as Chile saltpeter.

**Hydrogen nitrate ( $\text{HNO}_3$ ).** Hydrogen nitrate is very difficult to prepare because it is very unstable. It is always obtained in aqueous solution, and this solution constitutes ordinary *nitric acid*.

**Nitric acid: properties.** The concentrated nitric acid of commerce contains about 68 per cent of hydrogen nitrate and 32 per cent of water. Such a solution has a density of 1.4. When pure it is a colorless liquid, but it is frequently colored slightly brown, owing to decomposition products.



**Preparation of nitric acid.** Nitric acid can be prepared by a number of different methods, the most important of which are the following:

1. *Preparation from sodium nitrate.* When sodium nitrate is treated with concentrated cold sulfuric acid, no chemical action seems to take place. If, however, the mixture is placed in a retort *A* (Fig. 94) and a gentle heat applied, nitric acid is given off as a vapor and may be condensed to a liquid by conducting the vapor into a tube *B* surrounded by ice water, as shown in Fig. 94. An examination of the liquid left in the retort shows that it contains sodium acid sulfate ( $\text{NaHSO}_4$ ), half of the hydrogen of sulfuric acid having been replaced by sodium. The equation for the reaction is as follows:

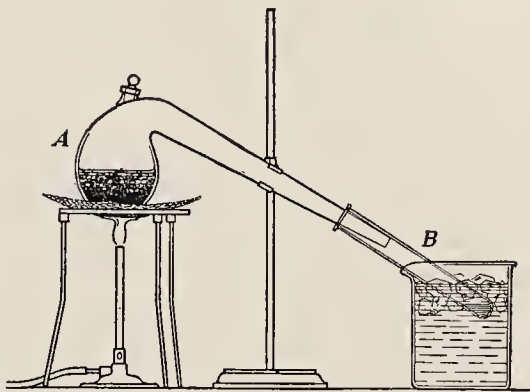
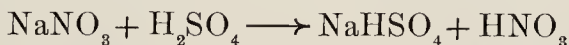
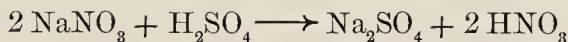


FIG. 94. Diagram of apparatus used in the preparation of nitric acid in the laboratory



If a smaller quantity of sulfuric acid is taken and the mixture is heated to a high temperature, normal sodium sulfate is formed:



In this case, however, the higher temperature required decomposes a part of the nitric acid, so the process is not economical.

2. *Preparation of nitric acid from the nitrogen of the air.* Since the supply of sodium nitrate is gradually diminishing, many efforts have been made to prepare nitric acid from the nitrogen of the air. There are two general ways of doing this:

*a.* The first consists in exposing a mixture of nitrogen and oxygen to the action of an electrical discharge. As a result a small percentage of oxides of nitrogen is formed. This can be

increased by having the mixture pass through an electric arc which has been drawn out to a great size by magnets (Fig. 95).

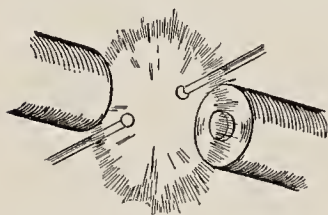


FIG. 95. Form of the electric arc employed in the Birkeland and Eyde process

The oxides so obtained combine with water to form dilute nitric acid. This method for preparing nitric acid (known as the Birkeland and Eyde process) has come into extensive use in recent years in Norway, since the necessary electrical energy can be generated at a very low cost by the waterfalls abounding in that country.

The dilute nitric acid obtained is neutralized with lime ( $\text{CaO}$ ), and the resulting calcium nitrate is sold for use as a fertilizer under the name *air saltpeter*.

This combination of nitrogen and oxygen is also brought about by lightning discharges. It is estimated that by this means no less than 100,000,000 tons of nitrogen is brought into combination annually; the resulting compounds are carried to the earth through the action of rain and snow.

*b.* The better method consists in first converting the nitrogen of the air into ammonia. This can be done either by the Haber process (p. 220) or by a process which will be described later under the heading "Cyanamide." If now the ammonia mixed with air is passed over a catalytic agent (platinum is used) in a heated tube, nitric acid is formed through the oxidizing action of the air, thus:



**The commercial preparation of nitric acid.** In the United States, nitric acid is prepared on a large scale chiefly by the action of sulfuric acid on sodium nitrate, as explained in method 1 above. The details of the process are given in Fig. 96. With diminishing supplies of sodium nitrate it is probable that increasing quantities will be made by the oxidation of ammonia (see method 2, *b*), the method by which Germany prepares nearly all her supply at the present time.

**Chemical conduct of nitric acid.** The most important chemical reactions of nitric acid are the following:

1. **Acid action.** Nitric acid has all the characteristics of a *strong* acid. It changes blue litmus red and has a sour taste

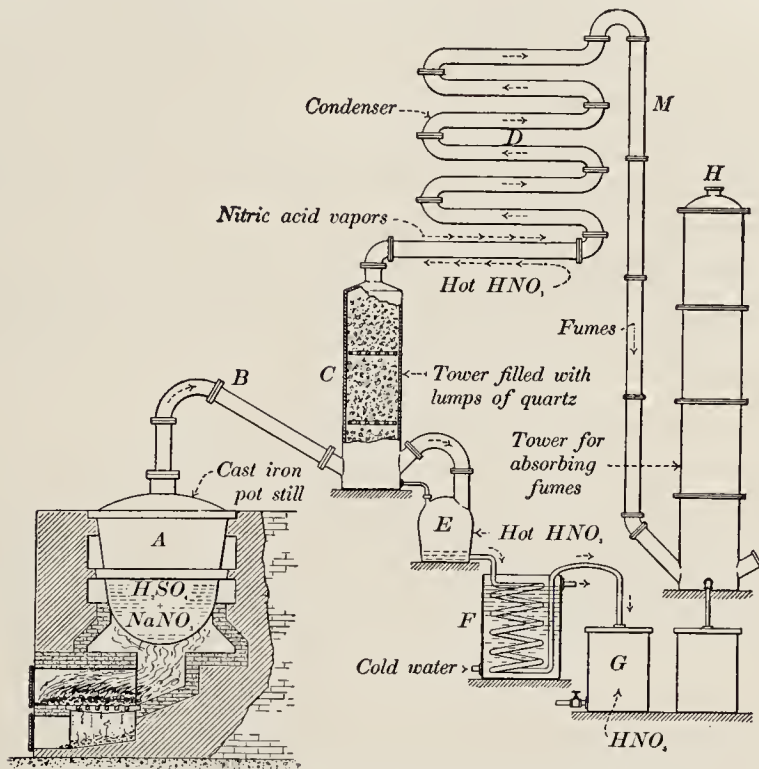
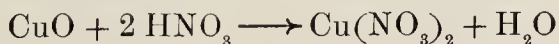


FIG. 96. Diagram of apparatus used for preparing nitric acid on a large scale from sulfuric acid and sodium nitrate

The sulfuric acid and sodium nitrate are heated in the iron pot *A*. The resulting acid vapors pass, in the direction indicated by the arrows, upward through the tower *C* into the condenser tubes *D*, where they are condensed. These tubes are inclined so that the nitric acid resulting from the condensation of the vapors runs back through the tower *C* into the vessel *E*. The acid is cooled by cold water in *F* and finally collects in the vessel *G*, from which it is drawn off. Any vapors not condensed in *D* pass down through the pipe *M* and are absorbed in the tower *H*

in dilute solutions. It gives the ions  $H^+$  and  $NO_3^-$  in solution and neutralizes bases, forming salts. It also acts upon the oxides of most metals, forming a salt and water; thus,

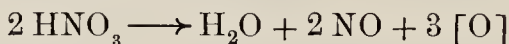


2. *Decomposition on heating.* When nitric acid is boiled or when it is exposed for some time to sunlight, it suffers a partial decomposition according to the equation

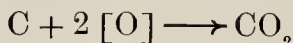


The substance  $\text{NO}_2$  (called nitrogen dioxide) is a brownish gas which is readily soluble in water and in nitric acid. It therefore dissolves in the undecomposed acid and imparts to it a yellowish or reddish color. Concentrated nitric acid highly charged with this gas is called *fuming nitric acid*.

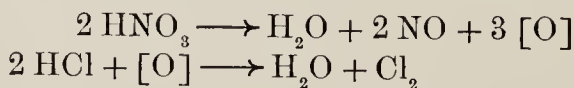
3. *Oxidizing action.* Because of its easy decomposition nitric acid is a good oxidizing agent. Under ordinary circumstances, when it acts in this way, the first step in the reaction takes place according to the equation



The oxygen is taken up by the substance oxidized and is not set free; this fact is indicated in the equation by placing the symbol for oxygen in brackets. Thus, if carbon is oxidized by nitric acid, the oxygen combines with carbon, forming carbon dioxide ( $\text{CO}_2$ ):



4. *Action on hydrochloric acid; aqua regia.* Since nitric acid is a good oxidizing agent, we might expect it to liberate chlorine from hydrogen chloride, and this is found to be the case.



A mixture of 1 part of nitric acid and 3 parts of hydrochloric acid is called *aqua regia* and is one of the strongest solvents known. It owes its solvent powers not to its acid properties but to the nascent chlorine which it liberates. Metals such as gold and platinum, which are not soluble in any of the common acids, readily dissolve in aqua regia, being converted into chlorides by the nascent chlorine.

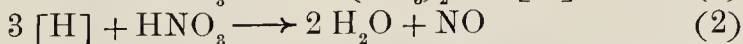
5. *Action upon metals.* All the metals, except gold, platinum, and a few other rare metals, are acted upon more or less readily by nitric acid. The action of the acid upon metals is complicated by the fact that it acts in two entirely different ways: (a) *In dilute solution* it acts chiefly as an acid; (b) *in concentrated solution* it acts as an oxidizing agent. The details of the reactions involved also depend upon whether the metal is above or below hydrogen in the electrochemical series (p. 216).

(a) *Action of metals above hydrogen.* In general we expect all *dilute* acids to evolve hydrogen with metals above hydrogen in the electrochemical series. It is probable that dilute nitric acid does this, yet experiment shows that very little free hydrogen is obtained. In its stead we obtain oxides of nitrogen, especially the gas having the formula NO.

A little reflection will show that this is just what we might expect, for nascent hydrogen is a strong *reducing* agent, while nitric acid is an equally strong *oxidizing* agent. Accordingly, if nascent hydrogen were to be liberated in contact with nitric acid, hydrogen would not be evolved as such, but would at once react with the acid, probably in the following manner:



In all such cases the complete reaction taking place may be illustrated by the following equations representing the reaction between zinc and nitric acid:

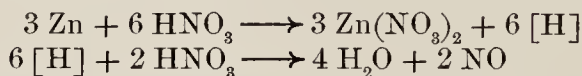


(The expression 2 [H] in equation (1) indicates that the hydrogen formed is not liberated as such, but as fast as formed reacts according to equation (2).)

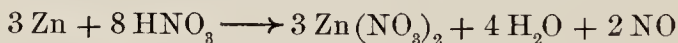
If *concentrated* nitric acid is used on these same metals, the action is similar to that which occurs with metals *below hydrogen* in the electrochemical series, as described in paragraph (b), on the next page.



**Combining equations.** It is often convenient to express in a single equation a reaction that really takes place in steps, such as that between zinc and nitric acid. This is readily done by combining equations (1) and (2) as given above. Before the equations are combined, however, they must be modified so as to express the fact that all the hydrogen represented as being formed according to equation (1) reacts with the nitric acid according to equation (2). This may be done by multiplying the first equation by 3 and the second equation by 2. The two equations will then be as follows:



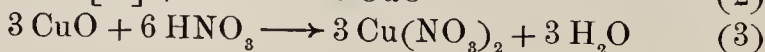
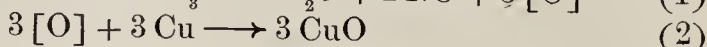
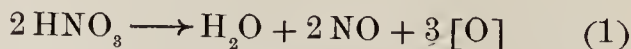
By canceling the common factor 6 [H], which represents the hydrogen formed in the one reaction and used up in the other, and then combining the equations, the following is obtained:



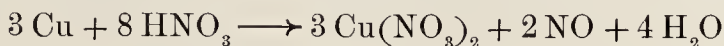
This complete equation has the advantage of making it possible to calculate very easily the proportions in which the various substances enter into the reaction or are formed in it. It is unsatisfactory in that it does not give full information about the way in which the reaction takes place.

(b) *Action on metals below hydrogen.* We do not expect acids to evolve hydrogen with metals below hydrogen in the electrochemical series (p. 216). If the metal is attacked at all, *it is first oxidized* and the oxide as fast as formed dissolves in an additional portion of the acid to form the corresponding salt. Of all the common acids, nitric acid acts most readily upon metals in this way.

Thus, with copper and nitric acid the reactions are represented by the following equations:



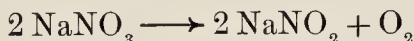
By canceling the factors  $3[\text{O}]$  and  $3\text{CuO}$ , which represent substances formed in one reaction and used up in another, and combining the three equations, we get the following:



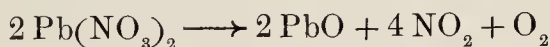
With *very* concentrated acid the product of the reactions is often the reddish-brown gas  $\text{NO}_2$  rather than the colorless  $\text{NO}$ . This is because *concentrated* nitric acid oxidizes nitric oxide ( $\text{NO}$ ) to nitrogen dioxide ( $\text{NO}_2$ ).

**Uses of nitric acid.** Nitric acid is used in very large quantities in the manufacture of explosives, of celluloid, and of dyes. It is a very important reagent in chemical laboratories.

**Salts of nitric acid; nitrates.** The salts of nitric acid are called *nitrates*. Many of these salts will be described in the study of the metals. They are all soluble in water and, when heated to a high temperature, undergo decomposition. In a few cases a nitrate, on being heated, evolves oxygen, forming a *nitrite*:

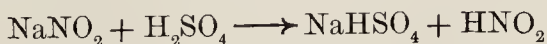


In most cases the decomposition goes farther, and the metal is left as an oxide:



The nitrates are especially used in the manufacture of gunpowder, sulfuric acid, nitric acid, and as a fertilizer.

**Nitrous acid ( $\text{HNO}_2$ ).** It is an easy matter to obtain sodium nitrite ( $\text{NaNO}_2$ ) by heating sodium nitrate, as explained in the previous paragraph. Now when sodium nitrite is treated with an acid, such as sulfuric acid, it is decomposed and nitrous acid is set free:



The acid is very unstable, however, and decomposes into water and oxides of nitrogen. Sodium nitrite is used in the manufacture of coal-tar dyes.

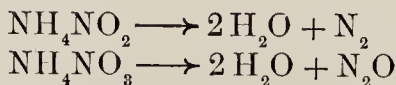
## OXIDES OF NITROGEN

The following table gives the names and formulas of the most important of the oxides of nitrogen, together with a brief statement of their properties:

Nitrous oxide ( $\text{N}_2\text{O}$ )	. . . . .	a colorless gas
Nitric oxide ( $\text{NO}$ )	. . . . .	a colorless gas
Nitrogen dioxide ( $\text{NO}_2$ )	. . . . .	a reddish-brown gas
Nitrogen trioxide ( $\text{N}_2\text{O}_3$ )	. . . . .	stable only at low temperatures
Nitrogen pentoxide ( $\text{N}_2\text{O}_5$ )	. . . . .	a white solid

**Nitrous oxide (laughing gas) ( $\text{N}_2\text{O}$ ).** Nitrous oxide is a colorless gas somewhat soluble in water, and in solution has a slightly sweetish taste. When inhaled it produces a kind of hysteria (hence the name *laughing gas*) and, if taken in large amounts, insensibility to pain, and unconsciousness. It was the first substance to be used as an anæsthetic in surgery and is still used in minor operations, especially those of dentistry. Nitrous oxide was first prepared by Priestley in 1772. Davy determined its composition in 1800 and was the first to point out the property which the gas possesses of rendering one temporarily unconscious when it is inhaled.

The most convenient method for its preparation consists in heating ammonium nitrate. Just as ammonium nitrite, when heated, yields water and nitrogen (p. 89), so ammonium nitrate decomposes in a similar way, forming water and nitrous oxide. The similarity between the two reactions is shown in the following equations:



Nitrous oxide is a very energetic oxidizing agent. Elements such as carbon, sulfur, iron, and phosphorus burn in it almost as brilliantly as in oxygen, forming oxides and setting nitrogen free. Evidently the oxygen in nitrous oxide is not held in very firm combination by the nitrogen.

**Nitric oxide (NO).** Nitric oxide is a colorless gas slightly heavier than air and nearly insoluble in water. It is most readily prepared by the action of nitric acid (density, 1.2) upon certain metals below hydrogen in the electrochemical series, such as copper (p. 216).

**Laboratory preparation.** The metal is placed in a flask *A* (Fig. 97) and the acid slowly added through the funnel tube *B*. The gas escapes through *C* and is collected over water. The gas at first evolved combines with the oxygen of the air contained in the flask to form the reddish-brown nitrogen dioxide, but this is dissolved as it bubbles through the water.

**Chemical conduct.** Nitric oxide is much more stable than nitrous oxide; yet it can be decomposed into its elements without difficulty.

If a bit of phosphorus is barely ignited and at once introduced into a jar of the gas, the flame is extinguished. If the phosphorus is heated to vigorous combustion and then introduced into the gas, the combustion continues with great brilliancy.

When nitric oxide comes into contact with oxygen or air, it at once combines with the oxygen, even at ordinary temperatures, forming a reddish-brown gas,  $\text{NO}_2$ , which is called *nitrogen dioxide*:

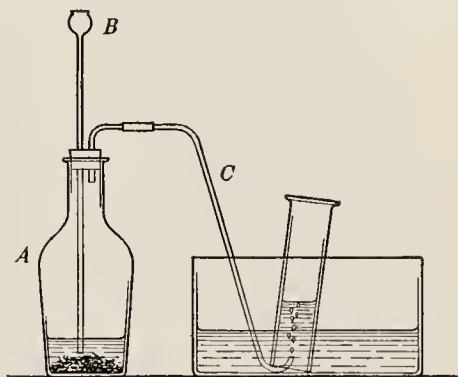
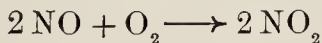
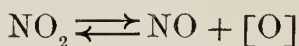


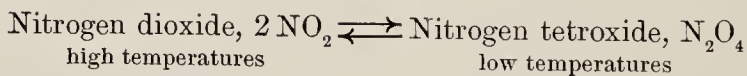
FIG. 97. Diagram of apparatus used in the preparation of nitric oxide

**Combination of nitric oxide with oxygen.** To show the formation of nitrogen dioxide from nitric oxide and oxygen, a tube is filled with the oxide and inverted in water, and pure oxygen is passed into it, as shown in Fig. 98. As each bubble of oxygen enters, it unites with the nitric oxide to form the reddish-brown dioxide. In a few minutes the color fades (because of the action of water upon the dioxide), and the water slowly rises in the tube.

**Nitrogen dioxide ( $\text{NO}_2$ ).** This gas is formed by the action of nitric oxide upon oxygen (p. 235); also by heating certain nitrates (p. 233). It has an unpleasant odor and is poisonous. It gives up a part of its oxygen to burning substances, acting as an oxidizing agent:

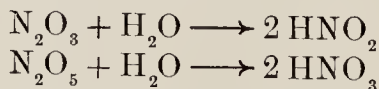


At higher temperatures the gas is reddish-brown in color. At lower temperatures it is pale yellow. This paler gas consists of double molecules,  $\text{N}_2\text{O}_4$ , and is sometimes called *nitrogen tetroxide*. At ordinary temperatures the gas is a mixture of the two kinds of molecules, and this fact may be expressed thus:



Two or more molecules of many other compounds combine in this same way under definite conditions.

**Acid anhydrides.** The oxides  $\text{N}_2\text{O}_3$  (nitrogen trioxide) and  $\text{N}_2\text{O}_5$  (nitrogen pentoxide) are rarely prepared and need not be separately described. When dissolved in water they combine with the water and form acids



Many other oxides act in the same way, combining with water to form an acid. Such oxides are called *acid anhydrides*. Thus,  $\text{N}_2\text{O}_3$  is called *nitrous anhydride*, while  $\text{N}_2\text{O}_5$  is *nitric anhydride*. An acid anhydride may therefore be defined as *an oxide that combines with water to form an acid*. Nearly all the oxides of the nonmetals are acid anhydrides.

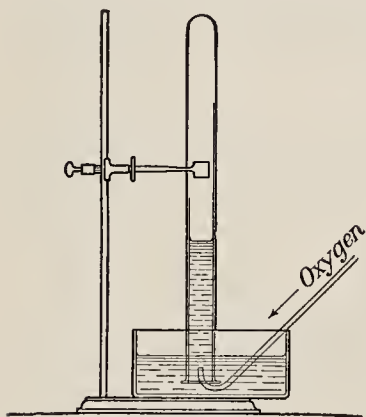


FIG. 98. The formation of nitrogen dioxide from nitric oxide and oxygen



## EXERCISES

1. Perfectly dry ammonia does not affect litmus paper. Explain.
2. Can ammonia be dried by passing the gas through concentrated sulfuric acid? Explain.
3. Ammonium hydroxide is a weak base; that is, it is not highly dissociated. When it is neutralized by strong acids, the heat of reaction is less than when strong bases are so neutralized. Suggest some possible cause for this.
4. Write the equations for the reactions taking place when ammonium hydroxide is neutralized by hydrochloric acid, by sulfuric acid, and by nitric acid respectively.
5. It is said that nitric acid is formed in the air during thunderstorms. Account for its formation.
6. What does the word *ammonia* mean? (Consult the dictionary.)
7. Why is nitric acid said to be a strong acid?
8. What are the properties of ammonia that make it suitable for use in the preparation of artificial ice?
9. Write the equations representing the reactions between ammonium hydroxide and sulfuric acid and between ammonium hydroxide and nitric acid, in accordance with the theory of electrolytic dissociation.
10. State the compounds and ions present in aqua ammonia.
11. What is meant by the statement "The reaction between water and ammonia is a reversible reaction"?
12. Why is it necessary to apply heat in the preparation of nitric acid from sodium nitrate?
13. (a) Give the steps in the production of nitric acid from air and water; (b) from air and hydrogen.
14. How many liters of ammonia at  $0^{\circ}$  and 760 mm. pressure will 1 liter of water dissolve? What would this volume of ammonia weigh? What weight of ammonium chloride would be necessary to prepare it?
15. (a) Calculate the weight of 1 liter of the concentrated nitric acid of commerce (p. 226). (b) What weight of hydrogen nitrate ( $\text{HNO}_3$ ) will this contain? (c) What weights of materials ( $\text{H}_2\text{SO}_4$  and  $\text{NaNO}_3$ ) are necessary for its preparation?
16. How many liters of nitrous oxide, measured under standard conditions, can be prepared from 10 g. of ammonium nitrate?

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17. What weight of copper is necessary to prepare 50 liters of nitric oxide?

18. What weight of sodium hydroxide is necessary to neutralize 1 liter of the concentrated nitric acid of commerce? Calculate the weight of the resulting compound.

19. 40 cc. of the concentrated nitric acid of commerce was added to 25 g. of zinc. After the reaction had ceased, the resulting mass was heated until the water present was all evaporated. Calculate the weight of the residue.

20. A compound on analysis was found to contain 30.44 per cent of nitrogen and 69.55 per cent of oxygen. Its molecular weight was found to be approximately 92. Calculate its formula.

21. (a) Calculate the percentage composition of nitrous oxide and of nitric oxide. (b) Show that the composition of these two oxides are in accord with the law of multiple proportion.

22. 100 g. of lead nitrate was decomposed by heat. Calculate the weight of the product left.

## CHAPTER XIX

### SPEED OF REACTIONS; REVERSIBLE REACTIONS; EQUILIBRIUM

**Speed of a reaction.** If the reactions that we have studied are attentively examined, it will be noticed that some go on very slowly, while others are very rapid. For example, Lavoisier found that tin must be heated in the air for days before an appreciable quantity of the oxide is formed. So, too, the action of acids upon pure zinc is very slow. On the other hand, when iron and sulfur have been heated to the temperature at which noticeable action begins, the action proceeds very rapidly. We express these facts by saying that reactions differ greatly among themselves *in their speed*. *By the speed of the reaction of one substance with another, or of the decomposition of a single substance, is meant the quantity of the given substance that undergoes change in a unit of time.* In the same way we measure the speed of all sorts of transactions in daily life. Thus, the speed of construction of a cement sidewalk may be measured by the weight of cement built into the walk per day.

**Factors that affect the speed of a reaction.** If we fasten our attention upon some particular reaction, we find that it may be made to go at very different speeds by changing certain of the conditions under which the reaction is proceeding. The most important of these are as follows:

1. **Temperature.** The most familiar way to hasten a reaction is to raise the temperature of the materials undergoing change. In ordinary combustion it is a familiar fact that the hotter the fire the faster the coal burns, while at ordinary temperatures the coal does not seem to oxidize at all, though there is plenty of oxygen in contact with it. It is probable

that even under these conditions there is *some* chemical action, but it is so slow that we cannot easily detect it. In general it has been found that a rise of  $10^{\circ}$  about doubles the speed of most reactions. Consequently, if we are in doubt as to whether two substances can act upon each other, we gradually raise the temperature of the mixture, knowing that this will increase the speed of action if any is taking place.

**2. Concentration.** It is evident that if we increase the quantity of oxygen in contact with the surface of a burning substance, we shall increase the speed of the combustion. For this reason substances burn much more rapidly in pure oxygen than in air, for the latter is only one fifth oxygen. The blacksmith pumps air into the forge to supply oxygen faster than it would be supplied by natural draft, and this operation amounts to increasing the quantity of oxygen available at any one time. We can express these facts by saying that the speed with which a given material burns depends upon the *concentration* of the oxygen.

Since reactions take place *between molecules*, it is clear that it is the increase in the number of *available molecules* that increases the speed of a reaction, rather than the weight in grams. *We shall therefore define concentration as the number of gram-molecules in a given volume of a gas or a solution.*

Instead of increasing the concentration of the oxygen, we may increase the surface of the burning substance. A log of wood burns more slowly than the same log split into kindling or worked into shavings. A lump of coal burns rather slowly ; but when finely powdered and suspended in the air as dust, it burns almost instantaneously and with explosive violence.

**Mass action.** If we burn a given weight of coal in the air, we shall, of course, get a definite weight of product and use up a definite weight of oxygen. But if we force into contact with the coal much more oxygen than can be used, the coal burns much faster. This effect of the excess of oxygen is called *mass action*. *We may define mass action as the effect*

*produced on the speed of a reaction by the presence of an available excess of one of the components taking part in the reaction.*

If, in a reaction, a great crowd of molecules *A* is present in comparison with a limited number of molecules *B*, it is clear that each molecule *B* will find one of *A* much faster than if the two were present in equal numbers, but that no more of the compound *AB* will be formed in the one case than in the other. A brick mason will build a given wall much faster if he has many more bricks at hand than if there are just enough and he has to move around to get them. So, in general, any reaction may be hastened by the mass action of one of the reacting substances.

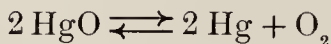
**3. Catalysis.** We have found that certain reactions go on much more rapidly in the presence of some material that does not seem to take any real part in the process, since it remains left over at the end. Such a substance is called a *catalyzer*, and its action is called *catalysis* (p. 29). Thus, at a given temperature potassium chlorate gives up oxygen more rapidly when manganese dioxide has been added to it than when the pure substance is heated (p. 29). Nitrogen combines with hydrogen much more rapidly in the presence of a catalyzer than in its absence (p. 222). A catalyzer reminds us of a lubricant in machinery. It makes the reaction proceed more rapidly, just as oil makes the machine run more easily.

It is probable that different catalyzers act in different ways, so that we shall never have a general theory of catalysis. For example, some appear to absorb great quantities of gases, in this way bringing them together with an enormous increase in concentration at one point. Others appear to take a real part in the first step of a reaction, but in a second step are restored to their original chemical condition, and so enabled to act again in an indefinite cycle.

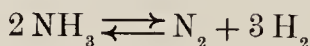
**Reversible reactions.** We have met with a number of reactions that are especially interesting, because by changing the conditions we can make them go in either direction at will. Thus, when we heat mercuric oxide we obtain mercury and



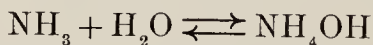
oxygen (p. 28), while if we heat mercury in contact with oxygen at a somewhat different temperature, we obtain mercuric oxide. These facts are represented in the following way:



In a similar way, we have found that when an electrical discharge is passed through a mixture of nitrogen and hydrogen we get a small quantity of ammonia, yet when the discharge is passed through ammonia we get a mixture of nitrogen and hydrogen (p. 220):



When ammonia is dissolved in water we have every reason for thinking that ammonium hydroxide is formed (p. 223), yet when we attempt to evaporate the solution to obtain this compound, it decomposes into water and ammonia:



Reactions of this kind are called *reversible reactions*.

**Equilibrium.** If we bring two substances together and measure the speed of their reaction with each other, it often appears to become slower and slower until it stops *before all the available materials have been used*. This seems singular, because the unused material is presumably just as available to enter into reaction as that which has already reacted.

It is easy to understand the facts just described, however, if we keep in mind a *kinetic picture* of the reaction. The reacting substances consist of vast numbers of molecules moving at all sorts of speed and in constant collision with each other. Some molecules, meeting under favorable conditions, act upon each other, and this gives rise to a reaction in one direction. But some of the molecules so formed may, by altered speed or by violent collision with other molecules, be restored to their original condition. This in reality sets up the reverse reaction.

In time a condition will be reached in which the changes taking place in the one direction will just compensate for those

in the other direction. The *average percentage* of each material present will then remain unchanged, though the individual molecules will keep on changing. This condition of affairs is called *equilibrium*. We may define *equilibrium* as *that condition in which the speed of two opposing reactions becomes equal*. Thus, ammonia, hydrogen, and nitrogen come to equilibrium in the presence of an electrical discharge when there is about 7 per cent of ammonia present, the percentage depending upon the temperature and the relative quantities of the gases originally mixed.

**Illustration.** This principle of equilibrium may be illustrated by the movements of people in a busy town. In the early morning nearly everyone on the street is moving in one direction toward business. Presently an increasing number are moving in the reverse direction, and by the middle of the morning about as many move in one direction as in the other. The population of the town may then be said to have reached equilibrium between those who are at home and those who are at work in the town.

**Changing the point of equilibrium by mass action.** When equilibrium has been reached, suppose we add an additional quantity of one of the acting substances, — say, hydrogen in the case just mentioned. This will enable the nitrogen to act more rapidly upon the hydrogen, for the two kinds of molecules will now meet more frequently. It will not at all affect the rate at which ammonia is decomposing, for this does not in any way depend upon the presence of hydrogen. The net effect will therefore be to bring about a new equilibrium in which a larger percentage of ammonia is present.

**Changing an equilibrium to a completed reaction.** If we arrange to withdraw the ammonia as fast as it is formed, before it has time to decompose, the reaction ought to go on until either the hydrogen or the nitrogen is used up. The ammonia can be so withdrawn if, during the discharge, we inclose the gases over water containing acid which will combine with the ammonia to form a soluble salt. In this case the reaction will

go on until one or the other reacting gases is used up. The equilibrium may therefore be changed into a completed reaction by withdrawing one of the components of the equilibrium as fast as it is formed.

**Equilibrium in solution.** In aqueous solutions we are interested chiefly in the equilibrium of ions. The molecules of an electrolyte keep dissociating into ions, while the ions, on meeting, recombine to form molecules, the result being an equilibrium between the two conditions. Thus, with nitric acid we have the equilibrium

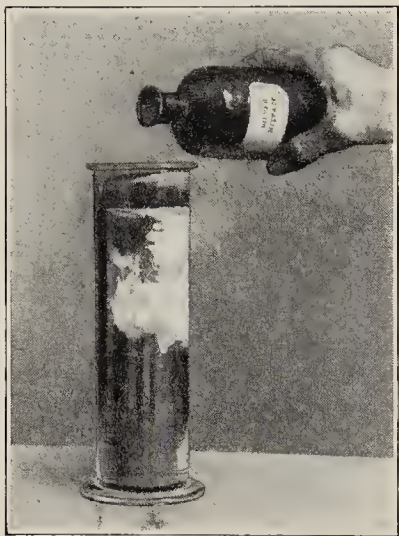
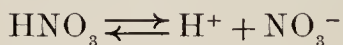


FIG. 99. When a solution of silver nitrate is added to hydrochloric acid, silver chloride is precipitated and the reaction goes to completion

we have present the ions  $\text{Na}^+$ ,  $\text{NO}_3^-$ ,  $\text{H}^+$ , and  $\text{SO}_4^{--}$ , together with the molecules  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaHSO}_4$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$ .

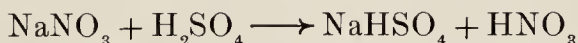
**Completion of reactions in solution.** The chemist makes use of reactions to secure various compounds in pure condition, and he wishes the yield to be as large as possible. Reactions which stop short of completion and end in an equilibrium are not suited to manufacturing purposes unless some means can be found of breaking up the condition of equilibrium and bringing the reaction to a definite conclusion. *There*

If we mix two electrolytes, the equilibrium that is reached is a much more complicated one, for *any* positive ion may unite with *any* negative one. At equilibrium all possible ions and combinations of ions will be present. Thus, when we mix sodium nitrate and sulfuric acid in the preparation of nitric acid (p. 227),

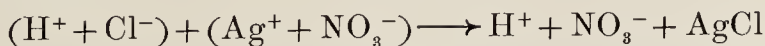
are, in general, three conditions under which reactions in solution may be brought quite or very nearly to completion.

1. **A volatile gas may be formed.** If the reaction is conducted under conditions such that one of the products is a gas *insoluble in the solvent*, the gas will make its escape as fast as it is formed. The reaction will then continue until one or the other of the ions taking part in the formation of the gaseous molecules is used up.

For example, when we mix sulfuric acid and sodium nitrate, no visible reaction takes place, though in reality an equilibrium in solution is set up. But if we heat the mixture above the boiling point of nitric acid, all this compound formed in the equilibrium between the two ions  $\text{H}^+$  and  $\text{NO}_3^-$  is converted into a gas, *insoluble in sulfuric acid*. The nitric acid distills away, more of the two ions unite, and the process goes on until all the  $\text{NO}_3^-$  ions are used up. We then have a completed reaction expressed in the equation



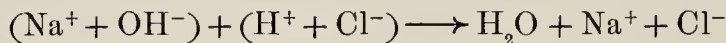
2. **An insoluble solid may be formed.** When hydrogen chloride ( $\text{HCl}$ ) and silver nitrate ( $\text{AgNO}_3$ ) are brought together in solution, we have the two kinds of molecules just named, the ions  $\text{H}^+$ ,  $\text{Cl}^-$ ,  $\text{Ag}^+$ ,  $\text{NO}_3^-$ , and the new combinations  $\text{HNO}_3$  and  $\text{AgCl}$ . One of these, namely, silver chloride ( $\text{AgCl}$ ), is insoluble in water and in acids, and as fast as it is formed it separates from the solution as a curdy white *precipitate* (Fig. 99). The reaction therefore continues until either the ion  $\text{Ag}^+$  or the ion  $\text{Cl}^-$  is used up, the completed equation being



3. **Two different ions may unite to form an undissociated molecule.** When we bring together in solution sodium hydroxide and hydrochloric acid, we have the ions  $\text{H}^+$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ , and  $\text{OH}^-$ . The  $\text{H}^+$  ions and the  $\text{OH}^-$  ions unite to form molecules of



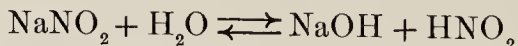
water *which do not again part into ions* save to a very slight extent. This leaves only the ions of NaCl in solution, the equation being



Neutralization is practically a completed reaction *because one of the products (water) is so little ionized*.

**The preparation of acids.** The principle explained in (1) is very frequently applied in the preparation of various acids. Most of the compounds that form acids in solution have rather low boiling points, while concentrated sulfuric acid has a rather high boiling point (338°). Consequently, if we take a salt of almost any common acid — a nitrate, a chloride, or an acetate — and treat it with concentrated sulfuric acid, at the same time heating the solution, the volatile acid will boil out of the mixture and can be condensed by cooling the vapor as in the preparation of nitric acid.

**Hydrolysis.** While water is very little ionized, nevertheless it forms *some* ions. Moreover, when a salt is dissolved in water to form a dilute solution, the relative mass of the water is very great. The reaction of neutralization is therefore reversed to a *slight extent*, forming a small amount of free base and of free acid, thus:



A reaction of this kind, *in which water acts upon a salt to form a base and an acid, is called hydrolysis*. It is the exact reverse of neutralization. If the base formed in hydrolysis is very weak and the acid is strong, the solution will turn blue litmus red, as is true with the salts of aluminum. If the base is very strong and the acid weak, the solution will turn red litmus blue, as is the case with many salts of sodium. If both the acid and the base formed are weak, then the compound may be *completely* hydrolyzed.



## EXERCISES

1. Mention some reversible reactions other than those given in this chapter?

2. Would silver nitrate produce a precipitate when added to a solution of sodium chloride (common salt)? If so, how would the precipitate compare in composition with that produced when silver nitrate is added to hydrochloric acid?

3. Barium sulfate ( $\text{BaSO}_4$ ) is a white insoluble compound much used as a pigment in making paints. Suggest a method for preparing it.

4. Is the reaction  $\text{NH}_3 + \text{H}_2\text{O} \longrightarrow \text{NH}_4\text{OH}$  reversible? If so, state the conditions under which it will go in each direction.

5. Is the reaction expressed by the equation  $2 \text{H}_2 + \text{O}_2 \longrightarrow 2 \text{H}_2\text{O}$  reversible? If so, state the conditions under which it will go in each direction.

6. The use of sulfuric acid in the preparation of nitric acid and hydrochloric acid is based on what property of the sulfuric acid?

7. Why is it necessary to apply heat in the preparation of nitric acid but not in the preparation of carbon dioxide?

8. When the salt  $\text{Al}_2(\text{SO}_4)_3$  is dissolved in water, the solution turns blue litmus red. Explain fully.

9. Carbonic acid has the formula  $\text{H}_2\text{CO}_3$ . Its sodium salt ( $\text{Na}_2\text{CO}_3$ ), when dissolved in water, changes red litmus blue. What conclusion do you draw as to the strength of carbonic acid?

10. If the speed of a certain reaction is doubled by a rise of  $10^\circ$ , how many times as great will the speed of the reaction be if it takes place at  $100^\circ$  than if it took place at  $0^\circ$ ?

## CHAPTER XX

### SOME COMPOUNDS OF CARBON

**Introductory.** In connection with the occurrence of carbon (p. 132), attention was called to the fact that this element is widely distributed in nature and that the number of its compounds is very large. Over 200,000 of them have been described, and many newly discovered ones are constantly being added to the list. Because of this large number, and also because certain characteristics distinguish the compounds of carbon from the compounds of other elements, it has been found convenient to group them under the general heading of *organic chemistry*, and to postpone their study until the introductory course in chemistry has been concluded. Nevertheless, even an introductory course must include a limited number of the more common compounds of carbon. A few of these will now be studied; others will be discussed in later chapters.

#### THE OXIDES OF CARBON AND CARBONIC ACID

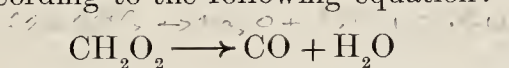
Carbon forms three oxides: namely, carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), and carbon suboxide (C<sub>3</sub>O<sub>2</sub>). They are all colorless gases. But little is known of the suboxide, and no further mention of it will be made. Carbon dioxide has been described in connection with carbon (p. 139). Of the three oxides, then, only the monoxide remains to be studied.

**Carbon monoxide (CO).** This compound is formed whenever carbon burns in a limited supply of air. It resembles carbon dioxide in that it is a colorless and nearly odorless gas. It differs from it in being very inflammable as well as very poisonous. *It is one of the most treacherous of poisons*, since its presence is

not revealed by the senses. Its poisonous properties are due to the following facts: The oxygen taken into our lungs is absorbed by the red coloring matter of the blood and thus carried to the various tissues of the body. Now this red coloring matter combines with carbon monoxide in preference to oxygen; hence, in an atmosphere containing even a small percentage of carbon monoxide, the blood soon loses its ability to absorb oxygen, and death results. A person undergoing slight exercise in an atmosphere containing as little as 0.2 per cent of the monoxide will become unconscious in about an hour, and if the inhalation of this small percentage continues for three hours, death will result.

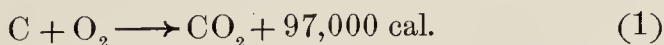
**Preparation.** Carbon monoxide can be made in a number of different ways, the most important of which are the following:

1. *By the decomposition of formic acid.* In the laboratory, carbon monoxide is usually prepared by heating formic acid. This is a liquid having the formula  $\text{CH}_2\text{O}_2$ . When heated it decomposes according to the following equation:

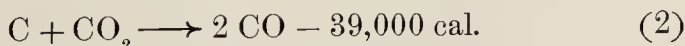


The decomposition takes place more smoothly in the presence of sulfuric acid, which absorbs the water formed. The gas is collected over water.

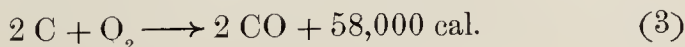
2. *By passing oxygen over hot carbon.* When oxygen is passed over carbon heated to its kindling temperature, carbon dioxide is first formed:



If the carbon is in great excess (or, in other words, if the supply of oxygen is insufficient for complete combustion), then the carbon dioxide at first formed is reduced to carbon monoxide by the hot carbon:



Combining equations (1) and (2), we have



The above reactions take place when hard coal burns in a stove. When the air first comes in contact with the hot coal, carbon dioxide is formed, but as this gas rises through the glowing coal it is reduced to the monoxide, which burns with a blue flame on the top of the coal, where it comes in contact with more air. If the supply of air is limited, then carbon monoxide passes off as one of the products of combustion (Fig. 100).

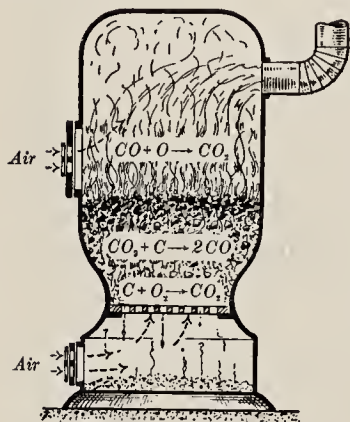
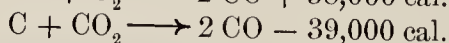
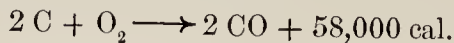


FIG. 100. Formation of carbon monoxide when hard coal is burned in a stove

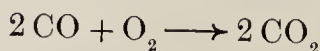
**Commercial manufacture of pure carbon monoxide.** During the World War large quantities of pure carbon monoxide were required for the manufacture of the poison gas known as *phosgene*. Pure oxygen cannot be used to advantage in the preparation of the monoxide on a very large scale, since the heat evolved is so great as to cause serious trouble. To

overcome this difficulty a mixture of oxygen and carbon dioxide was used in place of pure oxygen. Both these gases react with hot carbon to form carbon monoxide:



It will be seen from the above equations that the one reaction is exothermic, while the other is endothermic (p. 53). By mixing the two gases in the right proportion, therefore, the temperature of the furnace in which the reactions are carried out can be kept at any desired point.

**Chemical conduct.** Carbon monoxide burns in air or in oxygen with a blue flame, forming carbon dioxide.



It combines with chlorine to form the gas  $\text{COCl}_2$ , known as *phosgene* (p. 254). It also combines directly with some of the metals, as nickel and iron. Because of its affinity for oxygen

it is a good reducing agent. For example, when it is passed over hot copper oxide, the oxygen is withdrawn according to the following equation:



**The reducing power of carbon monoxide.** Fig. 101 illustrates a method of showing the reducing power of carbon monoxide. The gas is generated by gently heating some sulfuric acid in the flask *A* and then adding, a little at a time, formic acid through the

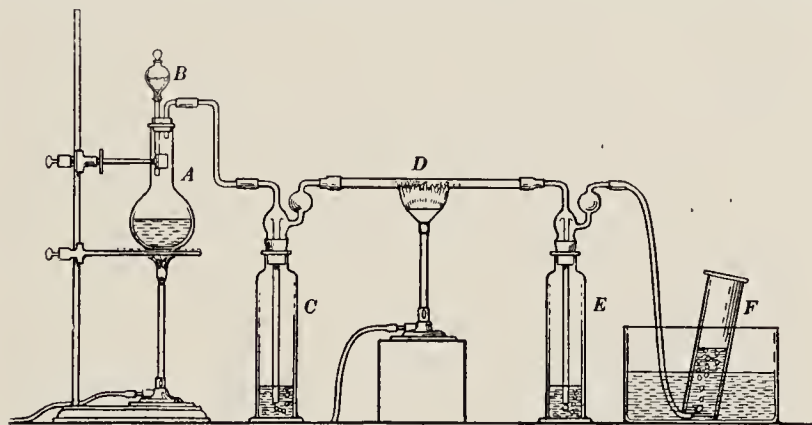


FIG. 101. Diagram of apparatus used in showing the reducing properties of carbon monoxide

funnel *B*. The bottle *C* contains a little water to wash the gas. *D* is a hard-glass tube containing copper oxide, which is heated by a burner. The black copper oxide is reduced to reddish metallic copper by the carbon monoxide, which is in turn changed to carbon dioxide. The formation of the carbon dioxide is shown by the precipitate in the calcium hydroxide solution in *E*. Any unchanged carbon monoxide is collected over water in *F*.

**Precautions against poisoning by carbon monoxide.** Since carbon monoxide is generated whenever carbon is burned in a limited supply of air, it is often formed in stoves when the air draft is shut off, especially when hard coal is used as a fuel. It is also formed when gas is burned in stoves and grates and the flame allowed to impinge against any cold object, such as

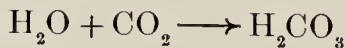


the metal used in the construction of the stove or the grate. *It is of the greatest importance, therefore, not only that all stoves and grates be provided with suitable chimney connections but that these connections be kept open; otherwise the carbon monoxide formed may escape into the air of the room and become a serious menace to anyone inhaling it. Many lives are lost each year because of this negligence.*

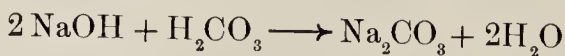
Carbon monoxide is also formed in the explosion of gasoline in gasoline engines. The exhaust gases of such engines contain from 4 to 12 per cent of the oxide. The air in a closed garage is rendered dangerous when an automobile engine is allowed to run for even a few minutes, and *many persons have lost their lives by working in a closed garage in which an engine is running.*

It is interesting to note that birds are very sensitive to this gas. In mine explosions carbon monoxide is always formed, and rescuers often carry canaries with them, the death of the birds warning the rescuers of their own peril.

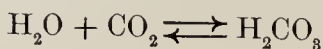
**Carbonic acid ( $\text{H}_2\text{CO}_3$ ).** In the discussion of carbon dioxide (p. 140) it was stated that the gas is somewhat soluble in water. As a matter of fact, when the gas is passed into water a certain amount of it combines with the water to form the compound known as *carbonic acid* ( $\text{H}_2\text{CO}_3$ ); for, like most of the oxides of the nonmetallic elements, carbon dioxide is an acid anhydride (p. 236).



The acid is, however, very unstable and cannot be isolated. Only a very small amount of it is actually formed when carbon dioxide is passed into water, as is evident from the small solubility of the gas. If, however, a base is present in the water, salts of carbonic acid are formed, and these are quite stable:



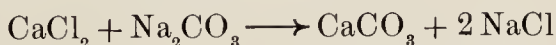
**Action of carbon dioxide on bases.** This conduct is explained by the principles of reversible reactions. The equation



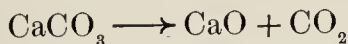
is reversible, and the extent to which the reaction progresses depends upon the relative concentrations of each of the three factors in it. Equilibrium is ordinarily reached when very little  $\text{H}_2\text{CO}_3$  is formed. If a base is present in the water to combine with the  $\text{H}_2\text{CO}_3$  as fast as it is formed, all the  $\text{CO}_2$  is converted into  $\text{H}_2\text{CO}_3$  and thence into a carbonate.

**Salts of carbonic acid; carbonates.** The carbonates form an important class of salts. Limestone, shells, and marble are largely calcium carbonate ( $\text{CaCO}_3$ ), common washing soda is sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), and baking soda is sodium acid carbonate ( $\text{NaHCO}_3$ ). Only the carbonates of sodium, potassium, and ammonium are soluble, and these can be made by the action of carbon dioxide on solutions of the bases, as has been explained in the preceding paragraph.

The insoluble carbonates are formed as precipitates when soluble salts are treated with a solution of a soluble carbonate. Thus, the insoluble calcium carbonate can be made by bringing together solutions of any calcium salt and any sodium salt. If calcium chloride and sodium carbonate are selected as the two salts, then calcium carbonate is formed in accordance with the following equation:

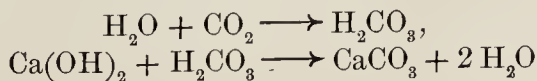


Most of the carbonates are decomposed by heating, yielding carbon dioxide and an oxide of the metal. Thus, calcium oxide (lime) is made by heating calcium carbonate (limestone), as follows:

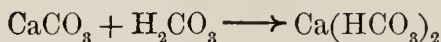


The carbonates are readily acted upon by acids, liberating carbon dioxide (p. 141).

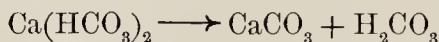
**Action of carbon dioxide on calcium hydroxide.** If carbon dioxide is passed into a solution of calcium hydroxide (limewater), calcium carbonate is at first precipitated (p. 141):



If the current of carbon dioxide is continued, the precipitate soon dissolves, because the excess of carbonic acid forms calcium acid carbonate, which is soluble:



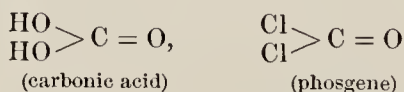
If now the solution is heated, the acid carbonate is decomposed and calcium carbonate once more precipitated:



**Carbonyl chloride (phosgene) ( $\text{COCl}_2$ ).** When a mixture of carbon monoxide and chlorine is exposed to the sunlight or is passed through a tube containing hot charcoal, the two gases combine to form the compound known as *carbonyl chloride* or, more commonly, as *phosgene*.

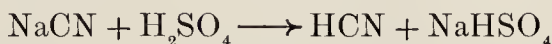


This is a very poisonous gas, easily condensed to a colorless liquid boiling at  $8^\circ$ . It is used in preparing certain dyes. Its structural relation to carbonic acid is shown in the following structural formulas:



**Cyanogen ( $\text{C}_2\text{N}_2$ ) and hydrogen cyanide ( $\text{HCN}$ ).** At high temperatures carbon unites with nitrogen to form the colorless, *very poisonous* gas cyanogen ( $\text{C}_2\text{N}_2$ ). With hydrogen and nitrogen it forms hydrogen cyanide ( $\text{HCN}$ ). This is a colorless liquid boiling at  $26^\circ$ . It has a peculiar odor suggesting peach kernels and is *extremely poisonous* either when its vapor is inhaled or when the liquid is taken internally. It is soluble in water in all proportions, forming the solution known as *hydrocyanic acid* or, more frequently, *prussic acid*. It is a very weak acid. Its salts are called *cyanides* and, like the acid itself, are very poisonous. Sodium cyanide ( $\text{NaCN}$ ) and potassium cyanide ( $\text{KCN}$ ) are white solids. Their solutions readily dissolve gold and are often used for extracting gold from its ores.

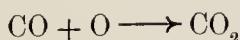
Since hydrogen cyanide is very volatile, it is easily liberated from the cyanides by the action of sulfuric acid (p. 246), and this is the usual method for preparing it:



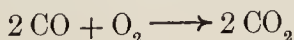
Because of its poisonous properties hydrogen cyanide is used to destroy insects, especially those that infest the citrus trees. Sometimes mills and stores become infested with animal organisms, and hydrogen cyanide is a very effective reagent for destroying them. Because of its poisonous properties it must be used with the greatest care. The federal government furnishes instruction for its use for the purposes mentioned.

**Solution of problems.** We have seen (p. 101) that a gram-molecular weight of any pure gas is the weight of 22.4 liters of the gas expressed in grams. By keeping this in mind it is possible for us to calculate in a very simple way the volume relations of gases entering into a reaction. All that we have to do is to write the equation so that each gas is represented in a molecular state. The number of gram-molecules of each gas entering into the reaction when multiplied by 22.4 gives the volume of the gas. The following problem will make the method clear: ,

What volume of oxygen is required to burn 100 liters of carbon monoxide? First write the simple equation for the reaction:



This, however, represents but 1 atom of oxygen; hence it must be doubled so as to represent a molecule of oxygen ( $\text{O}_2$ ):



This equation tells us that 2 gram-molecules of carbon monoxide, or 44.8 liters ( $2 \times 22.4$ ), will combine with 1 gram-molecule of oxygen, or 22.4 liters. In other words, 2 liters of carbon monoxide will combine with 1 liter of oxygen; hence 100 liters of carbon monoxide will combine with 50 liters of oxygen.

## EXERCISES

1. Determine the percentage composition of carbon monoxide and carbon dioxide.
2. Contrast the properties of carbon monoxide and carbon dioxide.
3. How could you prove that carbonic acid is formed when carbon dioxide is passed into water? What other gases have we studied that combine with water?
4. Why do most acids decompose carbonates?
5. What compound would be formed by passing carbon dioxide into a solution of potassium hydroxide? Write the equation.
6. Suggest a method for the preparation of ammonium carbonate.
7. Give the reasons why the reaction which takes place when calcium acid carbonate is heated completes itself.
8. Could a solution of sodium hydroxide be substituted for the solution of calcium hydroxide in testing for carbon dioxide?
9. Write the equations for the reactions that take place in the preparation of (a) hydrogen chloride, (b) hydrogen nitrate, and (c) hydrogen cyanide, and show that they are all the same in principle.
10. (a) What effect should you expect a solution of sodium carbonate to have on litmus? (b) What effect should you expect a solution of sodium cyanide to have on litmus?
11. What weight of formic acid is necessary for the preparation of 10 liters of carbon monoxide?
12. 100 liters of carbon monoxide, when burned, will give how many liters of carbon dioxide, both gases being measured under the same conditions of temperature and pressure.
13. Carbon dioxide was passed into an aqueous solution of 100 g. of sodium hydroxide until the base was all changed into sodium carbonate. How many grams of sodium carbonate were formed?



## CHAPTER XXI

### THE PERIODIC LAW ; STRUCTURE OF ATOMS

#### THE PERIODIC LAW

**Introduction.** By the time the atomic theory had been generally accepted more than 40 elements were known. There was every reason for believing that the total number of elements would turn out to be large (there are, in fact, 92). From the first it seemed to thoughtful chemists improbable that there should be so many entirely distinct forms of matter, and it was surmised that there must be some sort of relationship between the various elements. At least they would hardly be as diverse from one another as the elements we have been studying, but should form natural groups of closely related elements. The discovery of such groups would greatly simplify the study of chemistry.

**Döbereiner's triads.** The first natural grouping was observed by Döbereiner in 1829. He noticed that elements whose chemical properties were very similar were apt to show certain regularities in atomic weights. As a rule three such elements formed a group called a *triad*. Either the three atomic weights were very close together or there was an interval of about 40 units between every two weights, and the middle one was very nearly the arithmetical mean of the other two.

#### ILLUSTRATION OF DÖBEREINER'S TRIADS

Ca 40.07	Mg 24.32	Fe 55.84	Ru 101.7
Sr 87.63	Zn 65.38	Ni 58.69	Rh 102.9
Ba 137.37	Cd 112.41	Co 58.94	Pd 106.7

**Newlands's law of octaves.** For many years following the observation of Döbereiner, chemists studied the problem of classifying the elements according to atomic weights, and many remarkable groupings were suggested, but none of them included all the known elements. The main difficulty was that until about 1860 there was too much uncertainty as to the atomic weight that should be assigned to many of the elements.

In 1863–1865 Newlands showed that if we arrange the elements in the order of their atomic weights (omitting hydrogen), the first seven differ from each other very pronouncedly, but the next seven repeat the chief properties of the first seven, just as seven notes in the musical scale constitute an octave and succeeding notes repeat the same intervals. For three octaves among the elements the relations were very striking, but after that Newlands could not make the elements fit into appropriate places in his scheme.

**The periodic arrangement.** In the years 1869–1870 the Russian Mendeléeff and the German Lothar Meyer, quite independently of each other, advanced ideas very similar to those of Newlands (of which apparently they had not known), but they succeeded much better than Newlands in extending their arrangement to all the elements. The form of arrangement adopted by Mendeléeff and brought down to date is shown on page 259.

Omitting hydrogen and beginning with helium, the first eight elements are arranged in the order of their atomic weights in a horizontal row called a *series*. The ninth element, neon, greatly resembles helium in all its properties. It is therefore placed below helium as the first member of Series 2, the remainder of the series consisting of seven additional elements in the order of their atomic weights. The seventeenth element, argon, is a close relative of neon and is placed under that element, beginning Series 3, which concludes with the element manganese. If now we inspect the elements brought into *vertical* columns (called *groups*) by this arrangement, we find that

THE PERIODIC ARRANGEMENT OF THE ELEMENTS AND THE ATOMIC NUMBERS

Type of hydride	RH	RH <sub>2</sub>	RH <sub>3</sub>	RH <sub>4</sub>	RH <sub>5</sub>	RH <sub>2</sub>	RH	
Type of oxide	R <sub>2</sub> O	RO	R <sub>2</sub> O <sub>3</sub>	RO <sub>2</sub>	R <sub>2</sub> O <sub>5</sub>	RO <sub>3</sub>	R <sub>2</sub> O <sub>7</sub>	RO <sub>4</sub>
SERIES	GROUP I	GROUP II	GROUP III	GROUP IV	GROUP V	GROUP VI	GROUP VII	GROUP VIII
1	2 He = 4.00 Li = 6.94	3 Be = 9.02	4 B = 10.82	5 C = 12.000	6 N = 14.008	7 O = 16.0	8 F = 19.0	
2	10 Ne = 20.2	11 Na = 22.997	12 Mg = 24.32	13 Al = 26.97	14 Si = 28.06	15 P = 31.02	16 S = 32.06	
3	18 Ar = 39.94	19 K = 39.10	20 Ca = 40.07	21 Sc = 45.10	22 Ti = 47.9	23 V = 50.96	24 Cr = 52.01	25 Mn = 54.93
4	29 Cu = 63.57	30 Zn = 65.38	31 Ga = 69.72	32 Ge = 72.60	33 As = 74.96	34 Se = 79.2	35 Br = 79.916	
5	36 Kr = 83.9	37 Rb = 85.44	38 Sr = 87.63	39 Y = 88.92	40 Zr = 91.22	41 Nb = 92.91	42 Mo = 95.94	43 Ru = 101.7
6	47 Ag = 107.88	48 Cd = 112.41	49 In = 114.8	50 Sn = 118.7	51 Sb = 121.77	52 Te = 127.5	53 I = 126.932	44 Rh = 102.91
7	54 Xe = 131.3	55 Cs = 132.91	56 Ba = 137.36	57 La = 138.9*	58 Ce = 140.12	59 Pr = 140.91	60 Nd = 144.24	45 Pd = 106.7
8	79 Au = 197.2	80 Hg = 200.61	81 Tl = 204.39	82 Pb = 207.2	83 Bi = 208.98	84 Po = 210 (?)	85 (unknown)	46 Pt = 195.28
9	86 Rn = 222.	87 (unknown)	88 Ra = 226.97	89 Ac = (?)	90 Th = 232.12	91 Pa = (?)	92 U = 238.14	47 Ir = 193.1

\* Following lanthanum occurs a series of elements of atomic numbers 58-71. They closely resemble lanthanum and so cannot be distributed among the several groups. Their atomic numbers, symbols, and atomic weights are as follows: (58) Ce = 140.12; (59) Pr = 140.91; (60) Nd = 144.24; (61) Pm = 146.9; (62) Sm = 150.36; (63) Eu = 151.96; (64) Gd = 157.25; (65) Tb = 158.93; (66) Dy = 162.50; (67) Ho = 164.93; (68) Er = 167.26; (69) Tm = 168.93; (70) Yb = 173.04; (71) Lu = 174.96. These elements, together with lanthanum and hafnium, are known as the rare-earth elements.

those in each group are very similar to each other and constitute a triad like those of Döbereiner mentioned above.

The three elements following manganese (iron, nickel, and cobalt) interrupt the order so far followed. They have nearly the same atomic weight and resemble each other very closely. It would not do to distribute them in the first three groups, with which they have nothing in common, so they are placed in an additional vertical column (Group VIII). The element of weight next higher than cobalt is copper. If it is put into Group I, the elements following it fall into groups in which they evidently belong, and we finally obtain the complete table as shown on page 259.

**Relation of properties to atomic weights.** In any one *series* of elements the properties change progressively as we pass from element to element. Helium, at the beginning of the first series, possesses no chemical activity at all. Lithium is a univalent metal of very strong base-forming nature. Glucinum is a bivalent metal of a much weaker base-forming character than lithium, while boron has very few basic properties and is chiefly acid-forming. In carbon all base-forming properties have disappeared, and the acid-forming properties are much more pronounced than in boron. These become more emphasized as we pass through nitrogen and oxygen, until on reaching fluorine we have one of the strongest acid-forming elements. In base-forming and acid-forming properties these eight elements vary *regularly* with increase in their atomic weights.

**The periodic law.** If it were true that helium has the smallest atomic weight of all the elements and fluorine the greatest, so that in passing from one to the other we should include all the elements, we could say that the properties of the elements are progressively dependent on their atomic weights, or are *continuous functions* of them. But fluorine is an element of relatively small atomic weight, and we have seen that neon, which follows it, breaks the regular order and reproduces all

the characteristics of helium. Sodium, following neon, bears much the same relation to lithium that neon does to helium, and the properties of the elements in the second series repeat those of the elements in the first series until argon is reached, when another repetition begins. The properties of the elements do not vary *continuously*, therefore, with atomic weights, but at regular intervals there is a repetition, or *series*. This generalization is known as the *periodic law* and may be stated thus: *The properties of elements are periodic functions of their atomic weights.* x

**Two families in a group.** It has been noticed that after we pass the first two series the elements in every group (save Group 0) fall naturally into two subdivisions, or *families*. The elements in the odd-numbered series constitute family *A*, while those in the even-numbered series form family *B*. In all cases the elements in any one of these families are very intimately related in chemical character and in physical properties, while the relationship between elements in the same group but in different families is much less pronounced. Thus, the elements in family *A*, Group II, are the four closely related elements calcium, strontium, barium, and radium, and those in family *B* are zinc, cadmium, and mercury, a trio of very similar elements; but the resemblance between calcium and zinc or strontium and cadmium is much less pronounced.

The elements in the first two series stand a little apart from either of the two families in the group. Sometimes they are closely related to family *A*, as with lithium and sodium in Group I, and sometimes with family *B*, as with beryllium and magnesium in Group II.

**The atomic number.** Above the symbol of each element in the periodic arrangement (p. 259) is placed a numeral called the *atomic number*. With three exceptions these numbers are the same as the serial number of the element, beginning  $H = 1$ ,  $He = 2$ ,  $Li = 3$ . We shall see later on that they have a very fundamental significance.



**Family resemblances.** There are a number of respects in which we may confidently expect the elements *in a family* to resemble each other.

1. **Valence.** In general the valence of the elements in a family, as well as that of both families in a group, is the same, and the formulas of all corresponding compounds are therefore similar. If we know that the formula of calcium chloride is  $\text{CaCl}_2$ , we may be reasonably certain that all the elements in the family (as well as in the group) will be similar, not  $\text{SrCl}$  or  $\text{ZnCl}_3$ . The general formulas  $\text{R}_2\text{O}$ ,  $\text{RO}$ , etc. placed above the several groups indicate the probable formulas of the oxides of the elements in the group. The formulas  $\text{RH}$ ,  $\text{RH}_2$ , etc. show the composition of the compounds that we may expect the elements to form with hydrogen or with chlorine.

2. **Chemical conduct.** There is a regular gradation in chemical characteristics as we pass from element to element in a family, the elements of intermediate weight being intermediate in chemical characteristics. For example, potassium in Group I is a strong base-forming element, while cesium is much stronger; rubidium, intermediate in atomic weight, is about halfway between the others in chemical characteristics. Zinc in Group II is easily oxidized and is moderately easy to reduce from its oxide. Mercury is difficult to oxidize directly, and its oxide is reduced by merely heating it. Cadmium is intermediate between these extremes. All the elements in Groups I and II are typical metals. In the families of the succeeding groups the element at the top is likely to be acid-forming, but this property diminishes as we pass to elements of higher atomic weight, most of which are metals. Thus nitrogen, phosphorus, and arsenic in Group V are acid-forming, antimony forms both acids and bases, while bismuth is base-forming only. Hence nearly all the elements at the bottom of all the families have metallic properties.

3. **Physical properties.** In the same way the physical properties of the members of a family show a gradation as we

pass from element to element in the family. For example, the densities in the magnesium family are

$$\text{Mg} = 1.74, \quad \text{Zn} = 7.10, \quad \text{Cd} = 8.64, \quad \text{Hg} = 13.56$$

The melting points are

$$\text{Mg} = 651^\circ, \quad \text{Zn} = 419.4^\circ, \quad \text{Cd} = 320.9^\circ, \quad \text{Hg} = -38.87^\circ$$

**Value of the periodic law.** The periodic law has proved of great value in the development of chemistry.

1. *It has simplified study.* It is at once evident that such regularities greatly simplify the study of chemistry. A thorough study of one element of a family makes the study of the others a much easier task, since so many of the properties and the chemical reactions of the elements are similar. Thus, after we have studied the element sulfur in some detail, it is not necessary to study selenium and tellurium so closely, for most of their properties can be predicted with a fair degree of accuracy from the relation which they sustain to sulfur.

2. *It has predicted new elements.* When the periodic law was first formulated there were a number of blank places in the table which evidently belonged to elements at that time unknown. From their position in the table Mendeléeff predicted with great precision the properties of the elements which he felt sure would one day be discovered to fill these places. Three such elements—scandium, germanium, and gallium—were found within fifteen years, and their properties agreed in a remarkable way with the predictions of Mendeléeff. This is shown in the case of gallium as follows:

PROPERTIES OF GALLIUM	PREDICTED	FOUND
Atomic weight . . . . .	About 69	69.72
Melting point . . . . .	low	30°
Density . . . . .	5.9	5.95
Formula of oxide . . . . .	Ga <sub>2</sub> O <sub>3</sub>	Ga <sub>2</sub> O <sub>3</sub>
Action of air . . . . .	none	very slight

According to the table there are still some undiscovered elements, and great effort has been made to find them. This is particularly true of the two elements following manganese in family A, Group VII, whose weights should be approximately 100 and 187, and the element between radon in Group 0 and radium in Group II.

**3. It has indicated probable errors.** The physical constants obtained for many of the elements, as well as the atomic weights of some of them, did not at first agree with the values required by the periodic law, and a further study of such cases showed that in most cases errors had been made. The law has therefore been of great service in indicating probable error, and that is a good test of a theory or a law.

**Imperfections of the periodic table.** There has been a great improvement in the table since it was first published, but there still remain a good many features which are marked imperfections. Most conspicuous is the fact that the element hydrogen has no place in the table. There are three instances where elements must be transposed in order to make them fit into their proper places. According to their atomic weights argon should follow potassium, tellurium should follow iodine, and cobalt should follow nickel. Their properties show that in each case this order must be reversed to bring them into the proper families. The table separates some elements altogether which in many respects have closely agreeing properties. Iron, chromium, and manganese are in different groups, although they are similar in many respects. Following lanthanum in Group III, Series 7, are fifteen elements (known collectively as the rare-earth elements) before we reach hafnium, all of which are as close together as the members of any of the families, and all of which have a valence of three. They do not fit into the table in any natural way. As we learn more about the elements we shall no doubt be able to construct a table that will be even more striking in its presentation of relations and in its freedom from defects.

## THE STRUCTURE OF THE ATOM

**Introduction.** Early philosophers and chemists probably thought of an atom as a hard, spherical particle destitute of any internal structure and unchanging in size, shape, or mass. Many years ago, however, it became evident that an atom possessing such properties was wholly inadequate to account for the well-known facts of valence, ionization, and periodic relations. It became clear that the atoms of the various elements must be organized systems of some kind, but no direct evidence bearing upon the nature of these structures was secured until within the last two decades.

**Recent discoveries.** During the last few years discoveries have come so rapidly, and have been of such convincing character, that a flood of light has been shed upon the structure of the atoms. The experimental work that has given us these new ideas has been carried out by the methods of physics rather than by those of chemistry, and the student who wishes to follow the details of this work must seek information in a treatise on physics. All that can be attempted in this book is a brief sketch of ideas now generally accepted, with no attempt to describe the evidence supporting the ideas.

**Nature of electricity.** Until recently little was known about the nature of electricity, though much was known as to its effects, the laws it follows, its measurement, and its applications. We now know that electricity is made up of two fundamentally different electrical units. The names applied to these units and the mass of each unit are as follows:

1. **Negative electricity.** The units of negative electricity are called *electrons*. They are all of equal mass and are of about  $\frac{1}{1845}$  the mass of a hydrogen atom. They constitute the cathode rays generated when an electric current is passed through a vacuum tube, and the beta rays of radium (see radium).

2. **Positive electricity.** The units of positive electricity are called *protons*. In mass they are nearly equal to a hydrogen



atom, but in volume they appear to be even smaller than the electrons. They are millions of times more dense than any form of ordinary matter known to us. If a body contains an equal number of protons and electrons, then it is electrically neutral. If, on the other hand, a body contains an excess of one or the other of these electrical units, it is electrified. Electric current through a solid such as a copper wire is the motion of electrons.

**Electrical nature of the ordinary atoms.** The atoms of all the elements are composed of the two fundamental electrical units in equal numbers. The mass of the atom is largely dependent upon the number of protons it contains, since the mass of the electrons is almost negligible.

**The hydrogen atom.** The hydrogen atom is the simplest of all ordinary atoms. It consists of a single proton (positive charge), of mass approximately 1 (oxygen = 16 as standard), with a single electron revolving around it as a satellite, much as the moon revolves around the earth. The proton, carrying the mass of the atom, is often called the *nucleus* of the atom. Under some conditions the satellite electron can be knocked or pulled away from the nucleus, leaving a hydrogen nucleus with one positive charge (a proton) and no negative charge. In the gaseous state or in solution this constitutes a hydrogen *ion*. The hydrogen nucleus is thus regarded as identical with the atom of positive electricity and with the hydrogen ion.

**The helium atom.** The second element in the periodic arrangement, namely, helium, has an atomic weight of 4. Its atoms contain 4 protons and 4 electrons. The nucleus consists of the 4 protons and 2 electrons (negative), so that it has 2 positive *nuclear* charges. The other two electrons are held close to the nucleus in what is sometimes called the *polar position*. They cannot be readily pulled away from the nucleus, and we have no helium ions formed in solution like hydrogen ions. We shall see, however, that when an atom of radium explodes, helium atoms are projected from the radium with terrific



velocity (alpha rays), and these helium atoms have lost the 2 polar electrons and have double positive charges, constituting gaseous ions.

**The lithium atom.** Lithium, the third element in the periodic arrangement, has an atomic weight of 6.939. Its nucleus is made up of 7 protons and 4 electrons, and has therefore a positive charge of 3. Two more electrons occupy a polar position strongly bound to the nucleus, while the seventh electron revolves at a distance like the electron of hydrogen. It can be readily detached from the atom, forming the lithium ion with one positive charge.

**General structure of all atoms.** Instead of describing any more of the atoms in detail we may give the following general description: *All atoms are made up of protons and electrons. The total number of the protons and electrons present in any atom varies with the element, but the number of protons present in any one atom is always equal to the number of electrons present. Except in the case of the hydrogen atom all the protons present in any atom, and approximately half the electrons, are concentrated in the nucleus of the atom. Two of the remaining electrons are held in polar position while the rest revolve in definite orbits about the nucleus at a greater distance. The nucleus has small volume and great density, and, since it always contains approximately twice as many protons as electrons, is charged positively. Since the mass of the atom is largely concentrated in the protons, it follows that the number of protons in the nucleus of the atom of any element must be approximately equal to the atomic weight of the element. The volume of the whole atom is determined by the orbit of the outermost electron.*

**The determination of the nuclear charge ; the atomic number.** The brilliant young English physicist Moseley (killed in action at Gallipoli) discovered a remarkable spectroscopic method whereby the relative nuclear charges of the various atoms may be determined. By this method it has been found that the nuclear charge of the hydrogen atom is 1, that of

helium is 2, that of lithium 3, the nuclear charge of the atoms of the other elements increasing regularly with the atomic weight of the element. With a few exceptions these numbers representing the nuclear charges of the atoms of the different elements are the same as the serial number of the elements when the latter are arranged in the order of their atomic

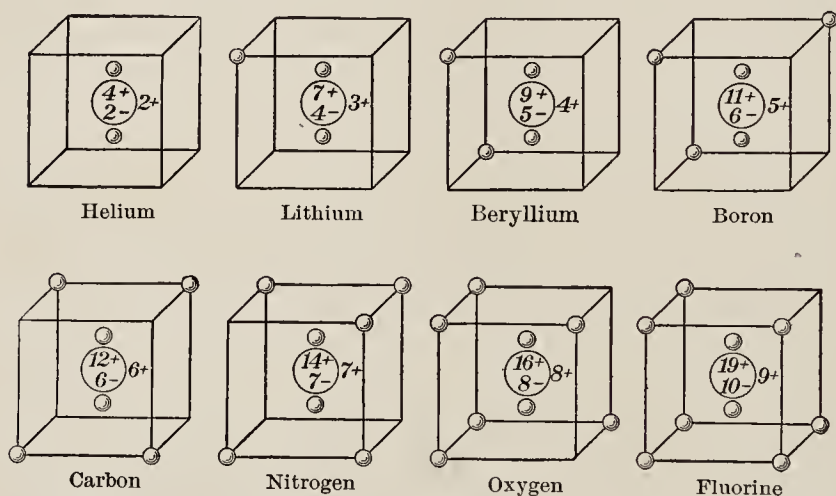


FIG. 102. Diagrams illustrating the Lewis and Langmuir conception of the structure of the atoms indicated

The nucleus of each atom is represented by a circle, and inside of this is given in each case the number of positive charges (protons), as well as the number of negative charges (electrons), in the nucleus. The excess of positive charges over the negative charges in the nucleus is indicated by the figure just outside the nuclear circle

weights as given in the periodic table. These numbers are called the *atomic numbers* and are placed above the symbols of the elements in the periodic table (p. 259).

It is very interesting to note that in the arrangement of the elements according to their atomic numbers argon comes before potassium, tellurium before iodine, and cobalt before nickel, in accord with the chemical properties of these elements, whereas the atomic weights reverse this order. The atomic number is therefore more fundamental than the atomic weight.

**The octet theory.** When we inquire into the way in which two atoms unite to form a compound, we meet with new problems. The physicists find good reason for supposing that the electrons revolve about the nucleus in various orbits and with great velocity, as we have already indicated. The chemist finds it much easier to explain chemical action by imagining that the electrons, while in motion, *retain an unchanging relation to each other*. So for all practical purposes they may be thought of as at rest or as vibrating about fixed positions. In time these different views will doubtless be brought into complete harmony with each other.

The American chemists Lewis and Langmuir have given most attention to the view that the electrons occupy *approximately fixed* positions around the nucleus. They suppose that as the satellite electrons increase in number they take up positions at the solid angles of a cube drawn around the nucleus as a center.

**Details of the octet theory.** The main points of the octet theory may best be shown by diagrams (Fig. 102) of the atoms of the elements. The hydrogen atom consists of 1 proton (the nucleus) and 1 electron occupying one of the solid angles of the imaginary cube surrounding the nucleus. The helium atom (Fig. 102) contains a nucleus made up of 4 protons and 2 electrons (thus giving a positive nuclear charge of 2), while 2 additional electrons occupy polar positions. The lithium atom, in addition to the nucleus and the 2 electrons occupying polar positions, has 1 electron occupying one of the solid angles of the cube. As the atomic number of the element increases, not only does the number of protons and electrons making up the nucleus increase, but also the number of electrons occupying positions at the solid angles of the cube. Thus, beryllium has 2 such electrons, boron 3, and carbon 4, as shown in the figures. When neon is reached (Fig. 103), all the eight angles are occupied. When we pass to the atoms of higher atomic number than neon, the additional electrons form a new shell outside of the completed octet, and the whole process repeats itself, as

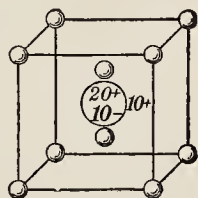


FIG. 103. The structure of the atom of neon

shown in Fig. 104, which represents the structure of the atom of chlorine. The inside cube, then, has relatively little influence in determining the properties of the atom. Atoms whose outer cubes

of electrons are similar in degree of completion, as fluorine (Fig. 102) and chlorine (Fig. 104), have similar properties.

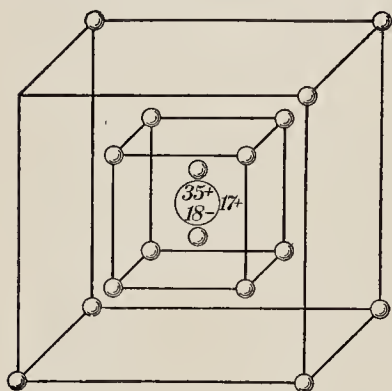


FIG. 104. The structure of the atom of chlorine

**Chemical combination.** Chemical combination may be thought of as taking place in either of two ways:

1. *By seizure of electrons to fill out octets.* An atom which has a nearly completed octet, such as fluorine (Fig. 102) or oxygen (Fig. 102), has a strong

tendency to seize electrons from other atoms which happen to have but few electrons in the outer satellite position. Thus, the fluorine atom with 7 electrons in its cube seizes the solitary satellite electron of the lithium atom to complete its cube, as shown in Fig. 105. This results in giving the fluorine a negative charge which holds the positive lithium nucleus in relatively loose combination.

In a dissociating solvent the two easily part into the lithium ion (+) and the fluorine ion (-).

The hydrogen atom presents a slightly different case. It consists of a nucleus and a single satellite electron, and so has no pair of electrons about the nucleus, as do all other atoms. When its electron is appropriated by the fluorine atom, the hydrogen nucleus adjusts itself to a position between its old electron and one of those of the fluorine octet. These two electrons constitute a pair close to the hydrogen nucleus and hold this

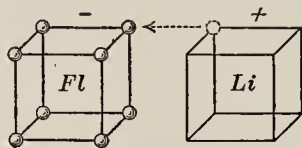


FIG. 105. Diagram illustrating the combination of the lithium atom and the fluorine atom

nucleus in rather close combination with the fluorine octet (Fig. 106). Consequently hydrogen fluoride is not so much ionized in solution as lithium fluoride.

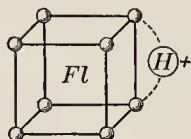


FIG. 106. Diagram illustrating the combination of the hydrogen atom and the fluorine atom

The oxygen atom with 6 electrons (Fig. 107) tends to seize 2 electrons to complete its octet. If it gets them from hydrogen atoms, we shall have the formula for water represented in Fig. 107.

2. *By sharing pairs of ions.* If each of two atoms has 4 or more electrons as outer satellites, neither one can rob the other of electrons to fill out its octet. Thus, the carbon atom (with 4 outer satellites) and 2 oxygen atoms (each with 6 outer electrons) combine to form carbon dioxide as represented in Fig. 108. Compounds of this general kind do not tend to ionize in solution.

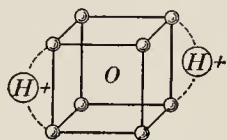


FIG. 107. Diagram illustrating the combination of hydrogen and oxygen atoms to form water

**The chemist's conception of an atom contrasted with that of the physicist.** As stated earlier in the chapter, the atom as conceived by the physicist is made up of a nucleus consisting of protons and approximately half as many electrons. About this nucleus other electrons revolve, each in its own fixed orbit. Under certain conditions an electron may jump from one orbit to another, and such changes are always attended by corresponding changes in energy. There is much to be said in favor of

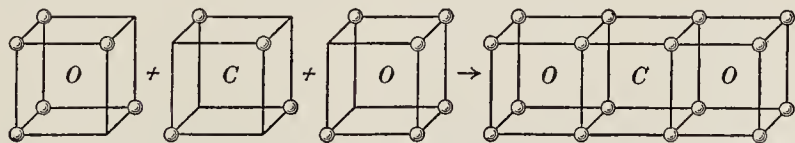


FIG. 108. Diagram illustrating the combination of carbon and oxygen atoms to form carbon dioxide

such a conception of the structure of the atom. Assuming that this view is correct, however, the chemist finds it difficult to explain many chemical phenomena. The Lewis and Langmuir octet



theory is the outgrowth of the effort to assume a structure that would be more in accord with the chemical facts. The two theories advanced in reference to the structure of the atom cannot, of course, both be true; in fact, it is more than probable that neither of them represents the exact structure. Undoubtedly, as additional knowledge is obtained, both of the theories advanced will be modified into a harmonious whole which will be accepted both by the physicist and by the chemist.

**The decomposition of atoms.** Since the atoms of all the elements are made up of the same material units, and differ only in the number and arrangement of these units, the question naturally arises, whether it may not be possible to obtain one element from another. For example, if we could find some means that would enable us literally to knock the atom into pieces, might not some of these pieces constitute the atoms of lower atomic numbers? As a matter of fact, when we come to study radium we shall find that this element (as well as certain other elements) is constantly undergoing decomposition, and that helium, the atom of which is very stable, is one of the products of decomposition. This decomposition of the radium atom takes place spontaneously, and no method of controlling it has been found. Many attempts have been made to decompose the atoms of other elements by subjecting them to powerful forces. Later we shall find that radium evolves certain rays; those known as the alpha rays are shot off with a velocity of 30,000 kilometers per second. By bombarding the atoms of elements with these alpha rays the English physicist Rutherford has succeeded in decomposing boron, nitrogen, fluorine, sodium, aluminum, and phosphorus, obtaining hydrogen as one of the products of decomposition. These remarkable results will undoubtedly lead to other important work along the same line.

**Isotopes.** It has long been noticed that a surprising number of elements have atomic weights that are very nearly whole numbers, although in many cases the weights are undoubtedly

fractional, as is true with chlorine. By the use of a remarkable method devised by Thomson, whereby the charged atoms of an element are subjected to the action of strong magnetic and electrical forces, it is possible to show that the elements of fractional weights are really composed of a mixture of atoms of different weights but in a constant ratio. Thus, magnesium, whose atomic weight is 24.32, is a mixture of *three different elements*, whose atomic weights are 24, 25, and 26, but whose chemical properties are identical, preventing a separation by chemical means. Similarly, chlorine (atomic weight, 35.458) is a mixture of two different elements of atomic weights 35 and 37 respectively. (Fig. 104, representing the structure of the chlorine atom, gives only the structure of that constituent whose atomic weight is 35.) *Such groups of atoms of different weights but identical chemical properties are called isotopes.* Thus ordinary magnesium is said to be composed of three isotopes. Many other elements are known to be mixtures of a number of isotopes, and a list of these is to be found on page 616. This list will doubtless be extended and possibly corrected by future investigations. It is evident that the isotopes of any element must always be present in the same proportion; otherwise the average atomic weight of the element would vary (p. 95), and this is not the case, at least so far as chemists have been able to determine.

**Valence.** From the standpoint of the octet theory *the valence of an atom is the number of electrons it has lost or gained in combining with another atom (or atoms), or the number of pairs of electrons shared with another atom (or atoms)* (Fig. 108). Thus, lithium (Fig. 102), in combining with another atom, loses 1 electron and so is left with a positive unit charge; hence it is said to have a positive valence of 1. In the same way boron has a positive valence of 3 (Fig. 102). Nitrogen may lose 5 electrons or gain 3; hence it has either a positive valence of 5 or a negative valence of 3. Oxygen most readily gains 2 electrons and so has a negative valence of 2.

## CHAPTER XXII

### THE SULFUR FAMILY

**Members of the sulfur family.** The three elements, sulfur, selenium, and tellurium, constitute the sulfur family. Sulfur is well known, and selenium resembles it in many of its properties, as well as in its chemical conduct. While tellurium does not show this marked similarity, nevertheless its compounds are closely related in composition to those of sulfur.

#### SULFUR

**Introduction.** Most people are sufficiently familiar with sulfur to recognize the yellow solid when they see it, but few are aware of its extreme importance to civilization both in peace and in war. In peace we depend upon its compounds for most of our insecticides to protect fruit and vegetables from insect ravages, for the refining of petroleum, and for the manufacture of soap, paper, matches, explosives for mining coal, dynamite for blasting rocks and making roads, and rubber for automobile tires and a host of other articles. In war we must add to this list the manufacture of nearly all explosives and of mustard gas, as well as the many military uses of rubber in masks, balloons, and surgical appliances. It is clear that it is a most important element.

Sulfur was one of the elements known from very early times. It is the brimstone of the Bible; it played a notable part in the speculations of the alchemists as to the nature of matter and its compounds.

**Properties of sulfur.** Ordinary sulfur is a pale-yellow solid without marked taste and with but a faint odor. It is

insoluble in water. It melts when heated, forming a thin, pale-yellow liquid. If the temperature is gradually raised, this liquid turns darker in color and becomes thicker until, at about  $235^{\circ}$ , it is almost black and is so viscous that a vessel containing it can be inverted without danger that the liquid will flow out. At higher temperatures it becomes mobile again, and at  $444.6^{\circ}$  boils, forming a yellowish vapor. When the hot sulfur is cooled, the same changes take place in reverse order.

**The occurrence of sulfur.** Sulfur occurs in nature both in the free state and in the combined state. Large deposits of the free sulfur occur in volcanic regions, especially in Sicily, and for many years these deposits constituted the chief source of the world's supply. In more recent years enormous deposits of sulfur have been found in Louisiana and Texas, with the result that the United States has now for a number of years been the chief sulfur-producing nation of the world. In 1924 the large sulfur mine in Louisiana was abandoned, so that at present all our sulfur comes from Texas.

In combination, sulfur occurs abundantly in the form of sulfides and sulfates. In smaller quantities it is found in a great variety of minerals and is a constituent of many vegetable and animal substances such as the proteid present in the yolk of eggs.

**The extraction of sulfur.** In Sicily the sulfur occurs mixed with rock and earthy materials. It is separated from these materials by piling up the crude sulfur in heaps and igniting it. The heat from the burning of a part of the sulfur melts another portion, which collects as a liquid at the bottom of the pile. This is drained off and purified by distillation in a retort (*A*, Fig. 109), the exit tube of which opens into a cooling chamber *B* of brickwork. When the sulfur vapor first

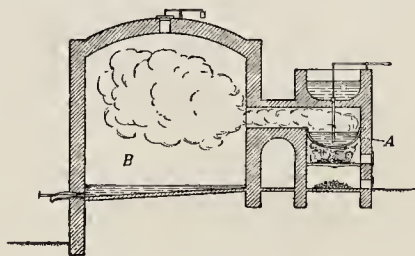


FIG. 109. Diagram of a sulfur still



enters the cold chamber it condenses as a fine, crystalline powder called *flowers of sulfur*. As the condensing chamber becomes warm the sulfur condenses in liquid form and is drawn off into cylindrical molds, the product being called *rolled sulfur* or *brimstone*.

In Texas, on the other hand, an entirely different system of extraction is followed. In this state the sulfur occurs in

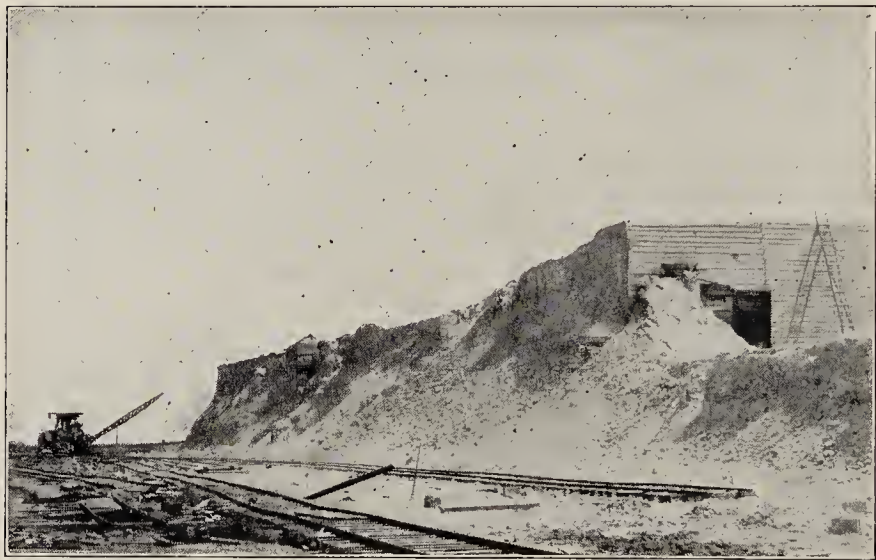


FIG. 110. A large block of sulfur stored for shipment

underground deposits, and these are covered with quicksand so that the sulfur cannot be mined directly. A typical one of these deposits lies at a depth of 700 feet, is circular in shape, and is about half a mile in diameter and 500 feet in thickness. The problem of mining these deposits was a subject of study for many years. The difficulty was finally solved by the American engineer Frasch about the year 1890. The method developed by Frasch consisted in sinking a well into the sulfur. The well is fitted with a system of pipes, one inside the other, and superheated water is then forced down between the pipes. The heat is sufficient to melt the sulfur in the vicinity of the



well, and the pressure exerted by the water forces the liquid sulfur to the surface of the earth. The liquid sulfur flows into wooden frames similar to those used in the construction of concrete walls, and then solidifies in very large blocks (Fig. 110). A single well has produced as much as 500 tons daily, and the product is 99.5 per cent pure. The production of sulfur in this way is limited only by the market demands. About 50 per cent of the output of sulfur is used for the manufacture of sulfuric acid.

**Varieties of sulfur.** Sulfur exists in a number of allotropic forms (p. 128) which are easy to obtain. The best known are the following:

1. **Ordinary, or rhombic, sulfur.** When sulfur crystallizes from solution in liquids (notably from carbon disulfide), it is obtained in compact yellow crystals which melt at  $112.8^{\circ}$  and have a density of 2.06. These crystals usually have 8 sides, belong to the rhombic system, and are known as *rhombic sulfur*. (See Appendix for the discussion of the different crystalline forms.) Sulfur is often found in a crystalline state in nature (Fig. 111), and these crystals always belong to the rhombic system. Brimstone is composed largely of rhombic sulfur.

2. **Prismatic, or monoclinic, sulfur.** When melted sulfur is allowed to cool until a part of the liquid has solidified, and the remaining liquid is then poured off, it is found that the solid sulfur remaining in the vessel is in the form of fine, needle-shaped crystals, which melt at  $119^{\circ}$  and have a density of 1.96. The needle-shaped form is called *monoclinic sulfur*, since the crystals belong to the monoclinic system.

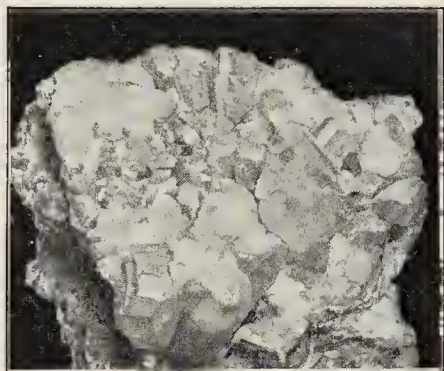


FIG. 111. Crystals of rhombic sulfur as they are found in nature

**Relation of rhombic to monoclinic sulfur.** Experiments have shown that whenever sulfur crystallizes at ordinary room temperature, the rhombic form is obtained; when crystallized at higher temperatures, as when the sulfur is melted and allowed to cool, the monoclinic form is obtained. Moreover, the temperature below which sulfur assumes the rhombic form and above which it assumes the monoclinic form is a perfectly definite one; namely,  $95.5^{\circ}$ . At this temperature, known as the *transition temperature*, the two forms of crystals remain unchanged when in contact with each other. If heated above  $95.5^{\circ}$ , the rhombic form gradually changes into the monoclinic form; if cooled below  $95.5^{\circ}$ , the monoclinic gradually changes into the rhombic form. This change of one form into the other ordinarily takes place very slowly, so that some days may pass before the change is complete.

**Amorphous sulfur.** In describing the properties of sulfur (p. 274), attention was called to the fact that sulfur is easily melted and forms a pale-yellow, mobile liquid, which at a higher temperature becomes dark and viscous. At intermediate temperatures the liquid obtained consists of varying quantities of the mobile liquid ( $S_{\lambda}$ ) and the viscous liquid ( $S_{\mu}$ ) in equilibrium with each other. If the melted sulfur is heated to boiling and poured into cold water, the sudden chilling prevents the crystallization of the viscous liquid, so that an amorphous, doughlike product is obtained. This form is insoluble in carbon disulfide and is known as *plastic sulfur*. It is largely the viscous sulfur ( $S_{\mu}$ ) in a very much undercooled state (p. 125). On standing, plastic sulfur changes in part into rhombic crystals.

The formation of plastic sulfur is shown in a very striking manner by distilling sulfur from a small, short-necked retort (Fig. 112) and allowing the distillate to run into cold water.

**Allotropic liquids.** It is a very common thing to find a solid, whether an element or a compound, that exists in two or more allotropic forms. Sulfur is the best-known case of a liquid that

exists in two forms, and in no other case is the difference between the two so striking and easily observed. It seems probable that liquid water consists of two kinds of molecules, namely,  $\text{H}_2\text{O}$  and  $(\text{H}_2\text{O})_2$ ; and it is possible that the fact that water reaches its greatest density at  $4^\circ$ , and below that temperature expands once more, is in some way connected with a shift in equilibrium between these two forms of water molecules.

**Chemical conduct of sulfur.** When sulfur is heated to ignition in oxygen or in the air, it burns with a pale-blue flame and forms sulfur dioxide ( $\text{SO}_2$ ). Small quantities of sulfur trioxide ( $\text{SO}_3$ ) may also be formed in the combustion of sulfur. Most metals when heated with sulfur combine directly with

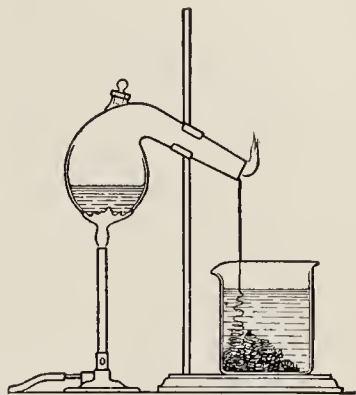


FIG. 112. Diagram of apparatus used in the preparation of plastic sulfur

it, forming metallic sulfides. In some cases the action is so energetic that the mass becomes incandescent, as has been seen in the case of iron uniting with sulfur. This property recalls the action of oxygen upon metals, and in general the metals which combine readily with oxygen are apt to combine quite readily with sulfur. Thus, iron is found in nature chiefly as the oxide  $\text{Fe}_2\text{O}_3$  and the sulfide  $\text{FeS}_2$ .

**Uses of sulfur.** Large quantities of sulfur are used in the manufacture of gunpowder, matches, vulcanized rubber, carbon disulfide, sulfur dioxide, sulfuric acid, and salts of various kinds. It is also used extensively in the manufacture of insecticides for use in orchards and vineyards.

**Lime-sulfur spray.** The chief sulfur insecticide is known as *lime-sulfur spray*. It is made by boiling sulfur with slaked lime; by this process a deep-red liquor is obtained which consists essentially of a solution of sulfides of calcium ( $\text{CaS}_4$  and  $\text{CaS}_6$ ). The liquid is a very efficient insecticide, particularly for scale, and it is also a fungicide.

## COMPOUNDS OF SULFUR WITH HYDROGEN

The following compounds of sulfur with hydrogen are known: hydrogen sulfide ( $\text{H}_2\text{S}$ ), a foul-smelling gas; hydrogen persulfide, an oily liquid from which the pure compounds  $\text{H}_2\text{S}_2$  and  $\text{H}_2\text{S}_3$  have been obtained.

**Hydrogen sulfide ( $\text{H}_2\text{S}$ ).** Hydrogen sulfide is often present in the vapors issuing from volcanoes. Dissolved in water it constitutes the so-called sulfur waters of common occurrence. It is formed when organic matter containing sulfur undergoes decay, and the disagreeable odor attending such changes is due in part to the presence of this gas.

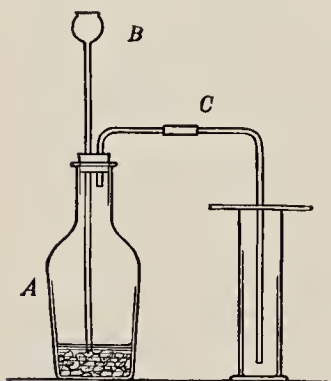
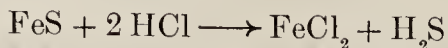


FIG. 113. Diagram of apparatus used in the preparation of hydrogen sulfide

**Properties.** Hydrogen sulfide is a colorless gas having a mild, disagreeable taste and an offensive odor. It is 1.18 times as heavy as air. When liquefied it boils at  $-59.6^\circ$  and freezes at  $-82.9^\circ$ . One volume of water at  $15^\circ$  dissolves 3.05 volumes of the gas. When this solution is heated to boiling, the gas is all expelled. In pure form it acts as a violent poison and, even when diluted largely with

air, produces headache, dizziness, and nausea. Fortunately its extremely disagreeable odor gives warning of its presence.

**Preparation.** Hydrogen sulfide is prepared in the laboratory by treating a sulfide with an acid. Iron sulfide ( $\text{FeS}$ ) and hydrochloric acid are usually employed:



**Laboratory apparatus.** A convenient apparatus is shown in Fig. 113. A few lumps of iron sulfide are placed in the bottle A, and dilute acid is added a little at a time through the funnel tube B. The gas escapes through the tube C and may be collected

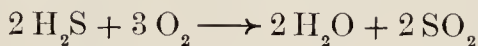


by displacement of air; or it may be passed into water, forming a solution. The Kipp generator (Fig. 16) is more convenient than the above apparatus if a larger quantity of the gas is desired.

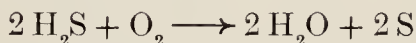
**Chemical conduct.** 1. *Acid properties.* In aqueous solution hydrogen sulfide is slightly ionized, giving hydrogen ions. The solution therefore acts as a weak acid and is known as *hydrosulfuric acid*. It possesses the general properties of an acid, turning blue litmus red and neutralizing bases with the formation of sulfides.

2. *Action of heat.* When heated to a high temperature hydrogen sulfide is decomposed into its elements, the speed of decomposition being marked at 500°.

3. *Action of oxygen.* At a high temperature hydrogen sulfide burns readily in either oxygen or air according to the equation



When there is not sufficient oxygen to combine with both the sulfur and the hydrogen, the latter element combines with the oxygen and the sulfur is set free:



When a solution of hydrogen sulfide in water is exposed to the air, the oxygen is insufficient for complete oxidation. The hydrogen of the sulfide unites with oxygen to form water, while the sulfur is liberated and settles to the bottom of the liquid. In this way are formed the deposits of sulfur found about many springs.

4. *Reducing action.* Because of the hydrogen present, together with the ease with which it is given up in contact with an oxidizing agent, hydrogen sulfide acts as a strong *reducing* agent. Thus, when it is bubbled through concentrated nitric or sulfuric acid, both of which are strong oxidizing agents, the hydrogen of the sulfide combines with a portion of the oxygen of the acid to form water, the acid being at the same time reduced.



A much-used method of drying gases consists in bubbling them through concentrated sulfuric acid, which absorbs the moisture. It is evident, however, from the statements just made, that this method cannot be used for drying hydrogen sulfide.

**5. Action on metals.** Hydrogen sulfide acts upon many metals, forming *sulfides*. Silver sulfide ( $\text{Ag}_2\text{S}$ ) is black, and it is owing to traces of hydrogen sulfide in the air that silver objects tarnish.

**Salts of hydrosulfuric acid ; sulfides.** The salts of hydrosulfuric acid, or sulfides, form an important class of com-

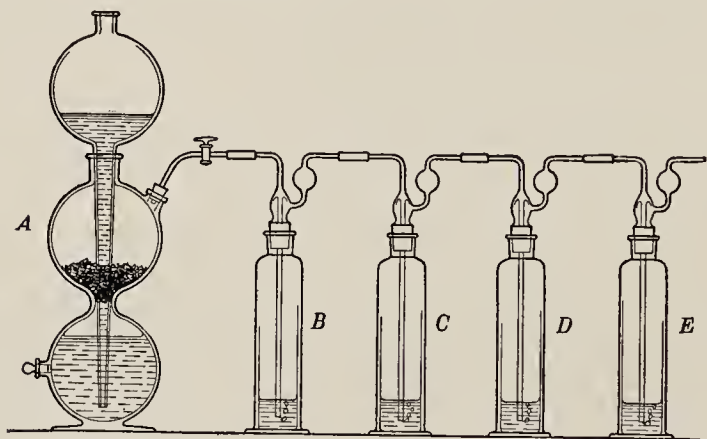
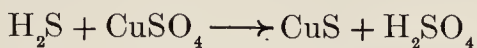


FIG. 114. Diagram of apparatus used in the preparation of insoluble sulfides by precipitation with hydrogen sulfide

pounds, and many occur in nature. They are all solids ; most of them are insoluble in water, while some are insoluble even in acids. As prepared in the laboratory, some of these salts, such as copper sulfide ( $\text{CuS}$ ) and silver sulfide ( $\text{Ag}_2\text{S}$ ), are black ; others, as cadmium sulfide ( $\text{CdS}$ ) and arsenic sulfide ( $\text{As}_2\text{S}_3$ ), are yellow ; while zinc sulfide ( $\text{ZnS}$ ) is white.

The soluble sulfides,  $\text{Na}_2\text{S}$ ,  $\text{K}_2\text{S}$ ,  $(\text{NH}_4)_2\text{S}$ , are most readily prepared by treating the appropriate base with hydrosulfuric acid ; the insoluble sulfides may be prepared by heating the metals with sulfur, although the general and more convenient method for their preparation consists in passing hydrogen sulfide into the aqueous solutions of appropriate salts of the

metals. Thus, copper sulfide may be prepared by dissolving copper sulfate ( $\text{CuSO}_4$ ) in water and passing hydrogen sulfide into the solution:



The copper sulfide, being insoluble, precipitates as fast as formed, and may be removed from the liquid by filtration.

**Laboratory preparation of sulfides.** The preparation of these sulfides as carried out in the laboratory may be illustrated in the following way: Hydrogen sulfide is generated in a Kipp apparatus *A* (Fig. 114) and is passed successively into bottles *B*, *C*, *D*, and *E*, containing, respectively, the aqueous solutions of silver nitrate, cadmium sulfate, zinc acetate, and sodium hydroxide. As the gas bubbles through the solutions there is formed black silver sulfide ( $\text{Ag}_2\text{S}$ ) in *B*, yellow cadmium sulfide ( $\text{CdS}$ ) in *C*, white zinc sulfide ( $\text{ZnS}$ ) in *D*. No precipitate is produced in *E*, for although sodium sulfide is formed, it is soluble in water and therefore does not separate.

### OXIDES AND OXYGEN ACIDS OF SULFUR

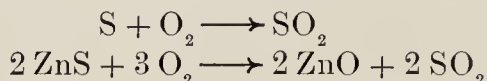
Sulfur forms five different oxides, of which the most important are sulfur dioxide ( $\text{SO}_2$ ) and sulfur trioxide ( $\text{SO}_3$ ). Both of these are acid anhydrides, uniting with water to form sulfurous acid and sulfuric acid respectively.

**Sulfur dioxide (sulfurous anhydride) ( $\text{SO}_2$ ).** This is the well-known gas resulting from the combustion of sulfur. It occurs in nature in the gas issuing from volcanoes as well as in solution in the waters of some springs.

**Properties.** Sulfur dioxide is a colorless gas and at ordinary temperatures is 2.2 times as heavy as air. It has a peculiar, irritating odor, familiar as the odor of burning sulfur matches. The gas is very soluble in water, 1 volume of water dissolving approximately 80 volumes of the gas under standard conditions. At  $-10^\circ$  it condenses to a colorless liquid largely used as a refrigerant in the iceless household refrigerators now coming into general use.

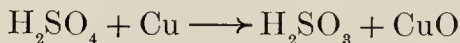
**Preparation.** Sulfur dioxide is prepared by three general methods :

1. *By the combustion of sulfur or a metallic sulfide.* In either case the sulfur is converted into sulfur dioxide :



The enormous quantities of sulfur dioxide used in the manufacture of sulfuric acid are prepared by this general method.

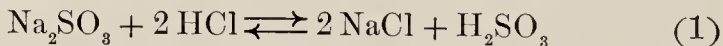
2. *By the reduction of sulfuric acid.* When concentrated sulfuric acid is heated with certain metals, such as copper, a part of the acid is reduced to sulfurous acid.



The latter compound then decomposes into sulfur dioxide and water, while the copper oxide is converted into copper sulfate. The complete equation is as follows :



3. *By the action of acids upon a sulfite.* Sulfites are salts of sulfurous acid ( $\text{H}_2\text{SO}_3$ ). When an acid, such as hydrochloric acid, is added to a sulfite, sulfurous acid is formed, which decomposes into water and sulfur dioxide. The reactions are expressed in the following equations :



**Explanation of the reaction.** In the action of hydrochloric acid upon sodium sulfite, as expressed in these equations, we have two reversible reactions depending upon each other. It might be expected that the reaction expressed in equation (1) would result in an equilibrium, since none of the substances represented in the equation are insoluble or volatile in the presence of water. The sulfurous acid, however, decomposes as fast as it forms, according to equation (2), the resulting sulfur dioxide escaping in the form of a gas. The reaction continues, therefore, until substantially all the sodium sulfite has been decomposed. Since sulfur dioxide is quite

soluble in water, it is evident that the reaction should be carried out in the presence of as little water as possible; otherwise a proportionately larger quantity of sulfur dioxide will remain in solution, and the reaction will not reach the same degree of completion.

**Chemical conduct.** Sulfur dioxide has a marked tendency to combine with other substances and is therefore an active substance chemically. It has a marked affinity for oxygen and is therefore a reducing agent. Under some conditions it can also act as an oxidizing agent. Thus, it reacts with hydrogen sulfide to form water and sulfur, as follows:



Since both hydrogen sulfide and sulfur dioxide are present in the gases issuing from volcanoes, it is probable that the large deposits of sulfur occurring in volcanic regions have resulted from the interaction of these two gases, according to the above equation. A characteristic property of sulfur dioxide is its conduct toward water, with which it combines to form sulfurous acid.

**Oxidation and reduction by the same reagent.** At first it may appear inconsistent to say that a given compound (such as sulfur dioxide) can act both as a reducing agent and as an oxidizing agent, but a little thought will show that this may easily be true. Any compound that contains oxygen *and is not too stable* may give up all or a part of its oxygen to another element or compound that has a very strong affinity for oxygen. On the other hand (as is true with sulfur dioxide), many oxides are able to take up more oxygen and form a higher oxide.

**Sulfurous acid ( $\text{H}_2\text{SO}_3$ ).** When sulfur dioxide is passed into water some of the gas combines with water to form sulfurous acid ( $\text{H}_2\text{SO}_3$ ), while the remainder is held in a state of solution. The sulfurous acid formed is in equilibrium, on the one hand with water and dissolved sulfur dioxide and on the other hand with the ions  $\text{H}^+$  and  $\text{HSO}_3^-$ , resulting from the ionization of a portion of the acid:



When heated this liquid acts as if it were simply a solution of sulfur dioxide in water, all the sulfur being evolved as sulfur dioxide. Toward a base, on the other hand, it acts simply as a solution of sulfurous acid (compare with aqua ammonia, p. 224).

Because of its unstable character sulfurous acid can be obtained only in the form of a dilute solution. This solution has the following properties:

1. **Acid properties.** The solution has all the properties typical of a very weak acid. When neutralized by bases sulfurous acid yields a series of salts called *sulfites*, most of which are insoluble in water.

2. **Reducing properties.** Solutions of sulfurous acid act as good reducing agents. This is due to the fact that sulfurous acid, like its anhydride,  $\text{SO}_2$ , has the power of taking up oxygen from the air or from substances rich in oxygen, and is changed by this reaction into sulfuric acid:

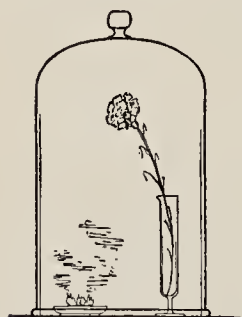
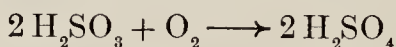


FIG. 115. Bleaching a flower with sulfur dioxide

3. **Bleaching properties.** Sulfurous acid has strong bleaching properties and is therefore used to bleach paper and straw goods. Even canned corn and dried fruits are sometimes bleached by this compound, but there has been much discussion as to whether its use for this purpose should be allowed. As a rule the bleaching is not permanent. It is not so efficient a bleaching agent as chlorine, and for this reason is used in bleaching only such materials as are injured by the action of chlorine.

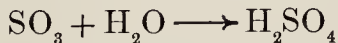
**Illustration.** The bleaching properties of sulfurous acid may be shown by bringing a small dish of burning sulfur under a bell jar (Fig. 115) in which has been placed a highly colored flower moistened with water. Straw hats may be cleaned and brightened in a similar way.



4. **Antiseptic properties.** Sulfurous acid has marked antiseptic properties, and on this account has the power of arresting fermentation. It is therefore used in certain foods containing sugars, such as sweet cider, canned corn, and dried fruits. Whether or not its use in foods should be permitted is a much-debated question.

**Salts of sulfurous acid; sulfites.** Since it contains two hydrogen atoms, sulfurous acid forms both acid and normal salts. Thus, with sodium it forms the salts  $\text{NaHSO}_3$  and  $\text{Na}_2\text{SO}_3$ . The sulfites are all solid substances and, like sulfurous acid itself, combine readily with oxygen, forming the corresponding sulfates. They are therefore good reducing agents. Because of this property, unless freshly prepared, they are apt to contain more or less of the corresponding sulfates. Calcium acid sulfite is used in the manufacture of paper from wood, since it dissolves the objectionable constituent (lignin) of the wood, leaving the pure cellulose, which is the material desired for the manufacture of paper.

**Sulfur trioxide (sulfuric anhydride) ( $\text{SO}_3$ ).** Sulfur trioxide is a colorless liquid which solidifies at  $16.83^\circ$  and boils at  $44.6^\circ$ . A trace of moisture causes it to solidify into a mass of silky white crystals somewhat resembling asbestos fiber in appearance. These crystals have the formula  $(\text{SO}_3)_2$  or  $(\text{S}_2\text{O}_6)$ . In contact with the air sulfur trioxide fumes strongly, and when thrown upon water it dissolves with a hissing sound and the liberation of a great deal of heat. The product of this reaction is sulfuric acid, so that sulfur trioxide is the *anhydride* of that acid:



**Preparation of sulfur trioxide.** When sulfur is burned in oxygen, minute quantities of sulfur trioxide are formed along with the sulfur dioxide. Likewise, when sulfur dioxide and oxygen are heated together, combination takes place, but the speed of the reaction is so slow that only traces of the trioxide

result. In the presence of a catalytic agent, however, such as finely divided platinum, the speed is greatly increased, and in this way sulfur trioxide can be obtained in quantities. The reaction is a reversible one, as is shown in the following equation :



The largest yield of sulfur trioxide is obtained when the reaction is carried out at approximately  $400^\circ$ ; at this temperature about 98 per cent of the sulfur dioxide combines with oxygen.

**Laboratory preparation.** The preparation of the trioxide by the last-named method can be carried out in the laboratory as follows: The platinum used as a catalytic agent is prepared by moistening

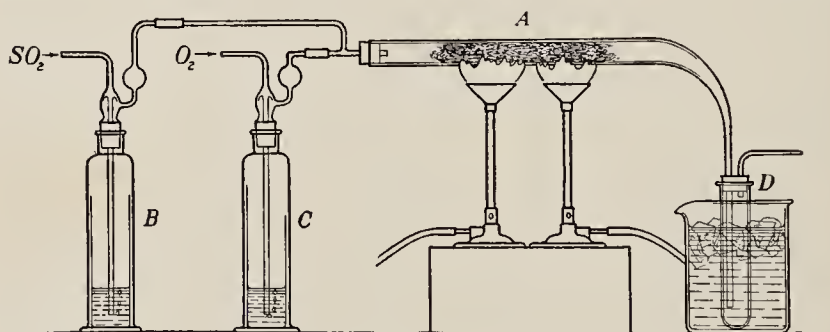


FIG. 116. Diagram of apparatus used in the preparation of solid sulfur trioxide

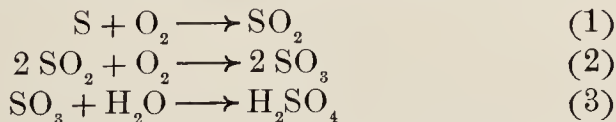
asbestos fiber in a solution of chloroplatinic acid and igniting it in a flame, whereby the platinum compound is reduced to metallic platinum. The fiber containing the finely divided platinum is placed in a tube of hard glass *A* (Fig. 116), which is then heated to about  $400^\circ$ , while equal volumes of sulfur dioxide and oxygen, previously dried by bubbling them through sulfuric acid (contained in bottles *B* and *C*), are passed into the tube. As this mixture comes in contact with the catalytic agent combination takes place and the resulting sulfur trioxide escapes from the jet at the end of the tube and may be condensed by surrounding the receiving tube *D* with a freezing mixture.

**Sulfuric acid ( $\text{H}_2\text{SO}_4$ ).** Sulfuric acid has long been known, and was one of the most important reagents employed by the alchemists. It is by far the most largely used of all the acids. The United States produces annually over 5,000,000 tons of the dilute acid (65 per cent  $\text{H}_2\text{SO}_4$ ) and nearly 1,000,000 tons of the more concentrated acid. Not only is it one of the most common reagents in the laboratory, but enormous quantities of it are consumed in the industries, especially in the manufacture of fertilizers, in the refining of petroleum, and in cleaning scale from iron and steel.

**Properties.** Pure anhydrous sulfuric acid, more properly named *hydrogen sulfate*, is a colorless, oily liquid nearly twice as heavy as water. The ordinary concentrated acid contains about 2 per cent of water, has a density of 1.84, and boils at  $338^\circ$ . It is sometimes called *oil of vitriol*, since it was formerly made by distilling a mixture of substances, one of which was called *green vitriol*.

**Manufacture of sulfuric acid.** Two general methods for the manufacture of sulfuric acid are in use at the present time. These are known as the contact process and the lead-chamber process.

**1. Contact process.** The reactions taking place in this process are represented by the following equations:



Sulfur dioxide is prepared according to equation (1) by burning sulfur or some sulfide (Fig. 117), such as iron pyrite ( $\text{FeS}_2$ ), in air. The resulting sulfur dioxide, together with sufficient air to furnish the necessary oxygen, is thoroughly scrubbed and dried, since the presence of impurities greatly diminishes the yield in the subsequent reaction. The mixed gases are then conducted through iron tubes filled with some porous material (asbestos or sodium sulfate), through which a suitable catalytic

agent, such as platinum or iron oxide, is interspersed, the material being kept at about  $400^{\circ}$ . Under these conditions sulfur trioxide is formed according to equation (2). The resulting sulfur trioxide is then absorbed in concentrated sulfuric acid.

**Historical.** The only part of the process which is difficult to carry out on a commercial scale is the formation of the sulfur trioxide. It has long been known that sulfur dioxide and oxygen

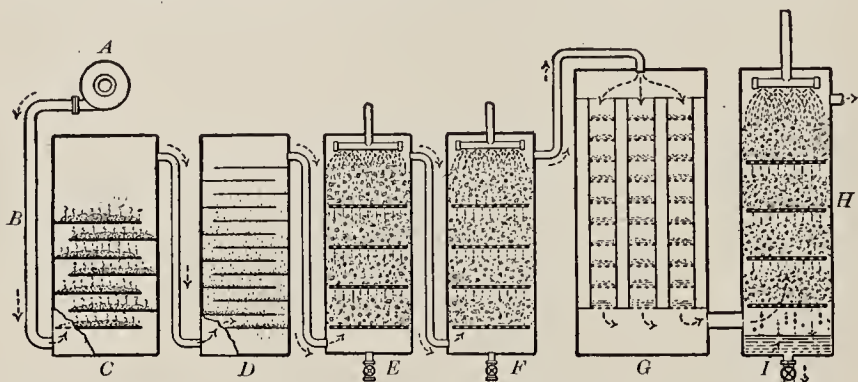


FIG. 117. Diagram to illustrate the commercial preparation of sulfuric acid by the contact process

The sulfur in the chamber *C* is burned by the air forced into the chamber by the blower *A*. The resulting sulfur dioxide and oxygen (air) is freed from dust by passing through the chambers *D* and *E* and dried by a spray of sulfuric acid in *F*. The gases are then passed over the catalyzer in *G*, where sulfuric trioxide is formed by the union of the sulfur dioxide and oxygen. The resulting sulfur trioxide is absorbed in the chamber *H*, by means of concentrated sulfuric acid, and the resulting product drawn off at *I*

combine when passed over finely divided platinum, but the cost of platinum, together with the poor yield of sulfur trioxide obtained, had made the process an impracticable one. A study of the conditions under which the reaction takes place resulted in improvements in the process, until finally, in 1901, the German chemist Knietzsch succeeded in overcoming the difficulties to such an extent as to make the process a commercial success for the manufacture of the pure concentrated acid. While platinum is the most effective catalytic agent for the process, it is very expensive, its commercial value being much greater than that of gold. This has led to the use of other catalytic agents, among which iron oxide appears to be the best, though it is inferior to platinum.

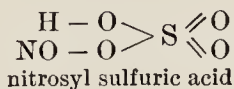
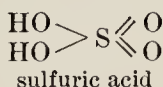


It is an interesting fact that the sulfur trioxide produced by this method will not combine with pure water. It is conducted into concentrated sulfuric acid and combines readily with the water present in this reagent.

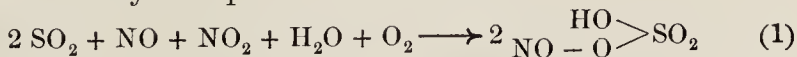
**2. Chamber process.** The older method of manufacture, exclusively employed until recent years and still the most important process, is much more complicated. The conversion of water, sulfur dioxide, and oxygen into sulfuric acid is accomplished by the chemical action of oxides of nitrogen. Since these oxides are gases, it is difficult to prevent their escape, and very elaborate precautions have to be taken to reduce the loss as much as possible. The reactions are brought about in large lead chambers, into which oxides of nitrogen, sulfur dioxide, steam, and air are introduced in suitable proportions. These react to form sulfuric acid, which collects on the floor of the chambers and is drawn off from time to time.

**Reactions of the chamber process.** The reactions involved are quite complex and are not at all thoroughly understood. It is believed, however, that the two following general reactions take place:

1. The substances introduced into the chambers first react to form a derivative of sulfuric acid known as *nitrosyl sulfuric acid*. The relation of these two compounds to each other may be seen from their structural formulas:

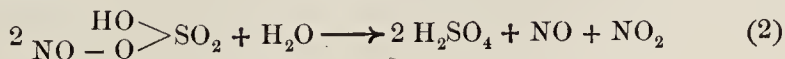


The reaction may be represented as follows:



This acid can be obtained in the form of white crystals known as *chamber crystals*.

2. In the commercial manufacture of sulfuric acid, however, such a separation does not occur, because sufficient water is always present to change the nitrosyl acid, as fast as formed, into sulfuric acid:





It will be noted that in equation (2) the same quantities of the oxides of nitrogen are formed as are required for equation (1). Theoretically, therefore, a small amount of these oxides should suffice to prepare an unlimited amount of sulfuric acid; practically, some of the oxides are lost, and this loss must be replaced.

**The sulfuric acid plant.** The simpler parts of a plant used in the manufacture of sulfuric acid are illustrated in Fig. 118. Sulfur or some sulfide, as  $\text{FeS}_2$ , is burned in the furnace *A*. The resulting sulfur dioxide, together with the necessary amount of

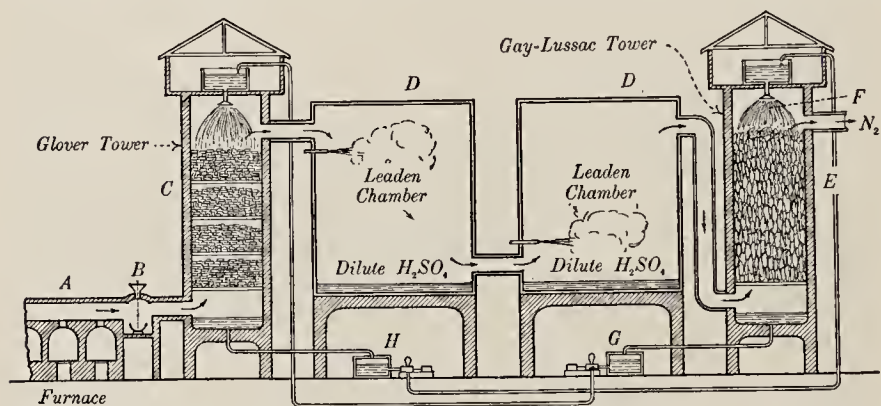


FIG. 118. Diagram to illustrate the commercial preparation of sulfuric acid by the chamber process

air, passes into the structure *C*, known as the Glover tower. In it the oxides of nitrogen are generated, as will be explained later, and these, together with the sulfur dioxide and air, pass into the chambers *D, D*. Water or steam is also introduced into these chambers at suitable points. Here the reactions take place which result in the formation of the sulfuric acid. The nitrogen remaining after the withdrawal of the oxygen from the air which entered the chamber escapes through the structure *E*, known as the Gay-Lussac tower. In order to prevent the escape of the nitrogen dioxide regenerated in the reaction, this tower is filled with pieces of acid-resisting rock or coke over which trickles concentrated sulfuric acid admitted in the form of a spray (*F*) at the top. The concentrated acid absorbs the nitrogen dioxide but not the nitric oxide, so that the latter escapes along with the nitrogen. The acid which is sprayed into the top of the tower collects in the bottom and is run off into the vessel *G*, from which it is forced

into the tank at the top of the Glover tower *C*. Here it is mixed with some dilute sulfuric acid and the mixture is sprayed into the top of the tower, which is partly filled with some acid-resisting rock. As the acid passes down through this material it meets with the hot gases entering from the furnace, whereby the nitrogen dioxide is liberated from the acid, passes over into the chambers *D*, *D*, and again enters into the reaction. During the process just described the dilute acid becomes sufficiently concentrated to serve again as an absorbent of nitrogen dioxide. The necessary quantity of it is therefore run into the vessel *H* from the bottom of the tower, and then forced into the tank at the top of *E*. In order to replace the oxides of nitrogen lost in the process, the necessary quantity is added by the action of sulfuric acid upon sodium nitrate in vessel *B*. The sulfuric acid so formed, together with the excess of condensed steam, collects upon the floor of the chambers in the form of a liquid containing from 62 to 70 per cent of hydrogen sulfate. The product is called *chamber acid* and is quite impure; but for many purposes, such as the manufacture of fertilizers, it needs no further treatment. It can be concentrated by evaporation in vessels variously made of lead, cast iron, an alloy of iron and silicon (duriron) or silicon dioxide.

**Relative advantages of the contact process and the lead-chamber process.** It will be noted that in the contact process it is just as easy to prepare the pure concentrated acid as the dilute acid. In the chamber process, however, the dilute acid is obtained first and can be prepared at a very low cost. The concentration and purification of the dilute acid is, however, an expensive operation. For these reasons the contact process can compete with the chamber process only in the manufacture of the pure concentrated acid.

**Chemical conduct of sulfuric acid.** Sulfuric acid possesses chemical properties which make it one of the most important of chemical substances.

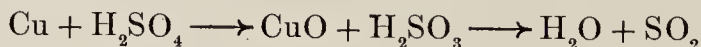
1. **Acid properties.** In concentrated aqueous solutions hydrogen sulfate forms the ions  $\text{H}^+$  and  $\text{HSO}_4^-$ , the latter, on further dilution of the solution, breaking down into the ions  $\text{H}^+$  and  $\text{SO}_4^{--}$ . It is this aqueous solution containing hydrogen ions which is properly termed sulfuric acid. It is one of the strongest of the common acids.

2. *Action as an oxidizing agent.* Sulfuric acid contains a large percentage of oxygen and is, like nitric acid, a very good oxidizing agent. When the concentrated acid is heated with metals, sulfur, carbon, or various other substances, oxidation takes place, the sulfuric acid decomposing according to the equation

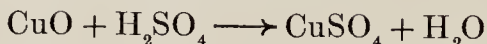


3. *Action on metals.* A *dilute solution* of sulfuric acid acts upon the metals that precede hydrogen in the electrochemical series (p. 216), forming a sulfate of the metal and hydrogen. Such a solution has no action upon the metals that follow hydrogen in the series save as the oxygen of the air first oxidizes the metal.

On the other hand, the *concentrated* acid acts upon a number of the metals without respect to their position in the electrochemical series; but in all these cases the first action is one of oxidation. With copper the reaction is represented by the equation



The copper oxide then dissolves in an additional quantity of sulfuric acid to form copper sulfate:



These two equations can be combined into the form



4. *Action on salts.* We have repeatedly seen that when a salt of a low-boiling acid is heated with an acid having a high boiling point, the low-boiling acid is liberated from its salt and expelled by the heat (p. 246). Now sulfuric acid has a higher boiling point than that of any of the common acids, and, being an inexpensive compound, it is admirably adapted to the preparation of other acids, such as hydrochloric and nitric.

5. *Action on water.* Concentrated sulfuric acid has a very great affinity for water, and when it is mixed with water

much heat is evolved. It is therefore an effective drying, or *dehydrating*, agent. Gases which have no chemical action upon sulfuric acid can be freed from water vapor by bubbling them through the concentrated acid.

**6. Action on organic substances.** Not only can sulfuric acid absorb water, but it will often withdraw the elements hydrogen and oxygen from a compound containing them, decomposing the compound and combining with the water so formed. For this reason most organic substances, such as sugar, wood, cotton and woollen fiber, and even animal tissues, all of which contain much oxygen and hydrogen in addition to carbon, are charred by the action of the concentrated acid. The process in general consists in the withdrawal of the oxygen and hydrogen present in the compound, thus leaving the black carbon as a residue.

**Salts of sulfuric acid; sulfates.** The sulfates constitute a very important class of compounds, and many of them have extensive commercial uses. The normal salts are all solids and, with the exception of those of barium, strontium, and lead, are soluble in water. Several others, notably calcium sulfate and silver sulfate, are only slightly soluble.

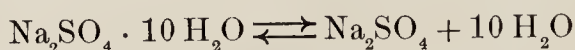
**Salt hydrates.** As a rule the crystals that we obtain on evaporating a solution of a salt do not correspond in formula to the simple salt, but consist of a compound of the salt with water. Thus, copper sulfate has the formula  $\text{CuSO}_4$ , but the blue crystalline compound (*blue vitriol*) that deposits from a solution of copper sulfate has the formula  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ . It is a compound formed by the union of 1 molecule of the sulfate with 5 molecules of water. Such a compound is called a *hydrate*, and the water which united to form the hydrate is referred to as *water of hydration* or *water of crystallization*. In a similar way ordinary sodium sulfate is the hydrate  $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ , and Epsom salt is  $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ . All hydrates have perfectly definite formulas.

A salt that is not hydrated, such as barium sulfate ( $\text{BaSO}_4$ ), or one from which all water has been driven off by heat, is



said to be *anhydrous*. Most soluble salts, when deposited from solution, are hydrated, and many are able to form two or more hydrates, according to the temperature at which they crystallize.

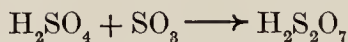
**Efflorescence.** All hydrates may be regarded as tending to lose water at ordinary temperatures, the reaction being reversible; thus,



For every hydrate there is a definite pressure of water vapor in the air that must be maintained upon the hydrate to keep up this equilibrium. If the water vapor normally present in the air exerts enough pressure, the hydrate is stable in the air; if it is not enough, the hydrate loses water in the form of vapor. In a small closed space, such as a bottle, this soon results in equilibrium. In the open air the hydrate loses its water and crumbles to powder. Crystals of the latter kind are said to be *efflorescent*. Hydrated sodium sulfate is an efflorescent salt.

**Other oxygen acids of sulfur.** In addition to sulfurous and sulfuric acids a number of other oxygen acids of sulfur are known, either in the free state or in the form of their salts. The following are the most important:

1. **Pyrosulfuric acid ( $\text{H}_2\text{S}_2\text{O}_7$ ).** This is a solid crystalline compound prepared by the union of sulfuric acid and sulfur trioxide:



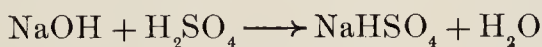
The acid and its salts are strong oxidizing agents. The *fuming sulfuric acid* of commerce consists of a mixture of sulfuric and pyrosulfuric acids.

2. **Persulfuric acid ( $\text{H}_2\text{S}_2\text{O}_8$ ).** This acid is unstable and exists only in dilute solution. Its salts, however, are stable. They are prepared by the electrolysis of concentrated solutions of the corresponding acid sulfates. Thus,  $\text{KHSO}_4$  by electrolysis yields  $\text{K}_2\text{S}_2\text{O}_8$ . The salts of persulfuric acid are very strong oxidizing agents. For example, ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) is often used as an oxidizing agent in connection with certain photographic processes.

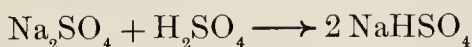


**Monobasic and dibasic acids.** Such acids as hydrochloric and nitric acids, whose molecules have *only one* replaceable hydrogen atom, or, in other words, yield one hydrogen ion in solution, are called *monobasic* acids. Acids whose molecules yield *two* hydrogen ions in solution are called *dibasic* acids. Similarly, we may have *tribasic* and *tetrabasic* acids. All the acids of sulfur that have been mentioned are dibasic acids. It is therefore possible for any of them to form both normal and acid salts.

**Preparation of acid salts.** The acid salts can be made in either of two ways: the acid may be treated with only half enough base to neutralize it,



or a normal salt may be treated with the free acid,

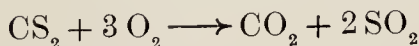


**Carbon disulfide ( $\text{CS}_2$ ).** When sulfur vapor is passed over highly heated carbon, the two elements combine, forming carbon disulfide:



Since heat is *absorbed* in this reaction, it must be supplied from external sources, and the reaction will proceed only at a rather high temperature.

Carbon disulfide is a heavy, colorless, highly refractive liquid which boils at  $46.3^\circ$ . When pure it has a pleasant odor, but it gradually undergoes slight decomposition and acquires a most disagreeable odor. Its vapor is very inflammable, burning in the air to form carbon dioxide and sulfur dioxide:



Carbon disulfide is a good solvent for many substances, such as gums, resins, and waxes, which are not soluble in most liquids, and it is therefore used as a solvent for such substances. It is also used as an insecticide, as a poison for vermin, and in the manufacture of carbon tetrachloride. Its vapor is poisonous as well as highly inflammable.

**Commercial preparation of carbon disulfide.** Commercially carbon disulfide is made by the direct combination of carbon and sulfur. In some plants the heat necessary for this union is derived from

an electric current, the process being carried out as follows: The main part of a large furnace *A* (Fig. 119) is filled with charcoal introduced through the trap *C*. Sulfur is added through the hoppers *D, D*. An electric current is passed in at *E, E*. The heat generated is sufficient to vaporize the sulfur, which then unites with the hot carbon to form carbon disulfide. The vapors escape at *H* and are condensed. Some of the furnaces are 40 ft. in height and yield as much as 25,000 lb. of the disulfide in twenty-four hours.

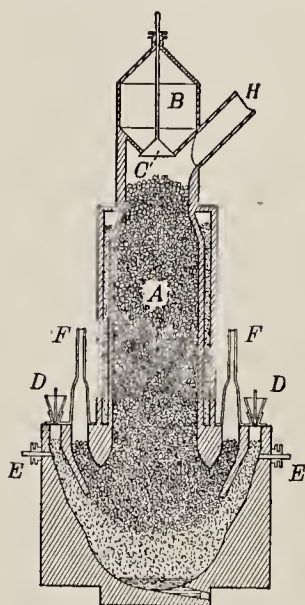


FIG. 119. Diagram of an electric furnace for the production of carbon disulfide

**Sulfur monochloride ( $S_2Cl_2$ ).** Three different chlorides of sulfur are known, the most important of which is *sulfur monochloride* ( $S_2Cl_2$ ). It is an oily, yellow liquid boiling at  $138^\circ$ . It fumes strongly in moist air and has a very disagreeable odor. It is made by burn-

ing sulfur in a current of chlorine and condensing the vapors so formed to a liquid. It is a good solvent for sulfur and is used in vulcanizing rubber. During the World War great quantities of it were used in the manufacture of the poisonous liquid known as mustard gas.

## SELENIUM AND TELLURIUM

**General discussion.** These two rather uncommon elements are so closely related to sulfur in their chemical conduct that we need not study them in detail. They are usually found associated with sulfur and sulfides, either as the free elements or, more commonly, in combination with metals. Thus, the only compound of gold that occurs in nature is gold telluride ( $AuTe_2$ ). Both selenium and

tellurium are associated with copper ores, and our supply of these elements comes from the copper refineries. The output is small but greater than the demand. Selenium is used in the glass industry (1) to neutralize the undesirable green color of glass made from impure sand and (2) to impart a ruby color to glass such as is used in automobile tail-lights. This element possesses the unusual property of being a good conductor of electricity in the light but not in the dark, — a property which promises to make the element of use.

With hydrogen, selenium and tellurium form compounds of the formulas  $H_2Se$  and  $H_2Te$ ; these bodies are gases with properties very similar to those of  $H_2S$ . They also form oxides and oxygen acids which resemble the corresponding sulfur compounds both in composition and in properties. The elements even have forms corresponding very closely to those of sulfur. Selenium oxychloride ( $SeOCl_2$ ) is a colorless liquid of promising importance as a solvent.

#### EXERCISES

1. Is the equation for the preparation of hydrogen sulfide a reversible one? As ordinarily carried out, does the reaction complete itself?
2. Suppose that hydrogen sulfide were a liquid; would it be necessary to modify the method of preparation?
3. Does perfectly dry hydrogen sulfide change the color of litmus paper? State reason for your answer.
4. What is an acid anhydride? Aside from those of sulfur, what other anhydrides have been mentioned?
5. How should you expect dilute sulfuric acid to act upon iron? upon silver? (Refer to electrochemical series.)
6. Can you suggest a reason why silver spoons become tarnished when in contact with certain kinds of food?
7. Mention other instances of catalysis aside from those given in this chapter.
8. In the commercial preparation of carbon disulfide what is the function of the electric current?
9. Write the equation representing the reaction between hydrosulfuric acid and sodium hydroxide; between hydrosulfuric acid and ammonium hydroxide.
10. Show that the preparation of sulfur dioxide from a sulfite is similar in principle to the preparation of carbon dioxide from a carbonate.

11. Write the names and formulas of the oxides and oxygen acids of selenium and tellurium.

12. Contrast the action of dilute sulfuric acid and of concentrated sulfuric acid upon zinc.

13. Write equations for the preparation of sodium acid sulfite by two different methods.

14. Calculate the weight of materials necessary for the preparation of sufficient hydrogen sulfide to saturate 20 liters of water at  $15^{\circ}$  and normal pressure.

15. What weight of sulfur is necessary for the preparation of 2000 lb. of sulfuric acid containing 5 per cent of water?

16. Suppose you wish to prepare 100 kg. of blue vitriol; calculate the weights of materials necessary for its preparation.

17. 50 g. of blue vitriol was dissolved in water, and hydrogen sulfide was passed through the solution until the copper was all precipitated. Calculate the weight of the precipitate.

18. How many calories of heat are absorbed in the preparation of 10 kg. of carbon disulfide?

19. Much of the sulfur dioxide used in the manufacture of sulfuric acid is prepared by the combustion of pyrite ( $\text{FeS}_2$ ). What weight of this sulfide would be required in a sulfuric-acid plant that has a daily output of 100 tons of acid containing 65 per cent of  $\text{H}_2\text{SO}_4$ , assuming that 10 per cent of the sulfur in the pyrite is lost in the operation?

20. Upon analysis a compound was found to have the following composition: sulfur, 39.07 per cent; oxygen, 58.49 per cent; hydrogen, 2.44 per cent. Calculate its formula.

21. Suppose you had as available raw materials sulfur and sodium chloride and wished to prepare 100 kg. of sodium sulfite daily. (a) What weights of the raw materials would be required? (b) What by-products would be formed in the process selected?

## CHAPTER XXIII

### THE CHLORINE FAMILY

NAME	ATOMIC WEIGHT	MELTING POINT	BOILING POINT	COLOR AND STATE
Fluorine (F) . . . .	19.00	— 223°	— 187°	pale-yellowish gas
Chlorine (Cl) . . . .	35.457	— 101.6°	— 34.6°	greenish-yellow gas
Bromine (Br) . . . .	79.916	— 7.2	58.7°	red liquid
Iodine (I) . . . .	126.932	113.5°	184.3°	purplish-black solid

**The family.** The four elements named in the above table form a strongly marked family of elements and illustrate very clearly the way in which the members of a family in a periodic group resemble each other, as well as the kind of differences we may expect to find between the individual members.

Compounds of all these elements save those of fluorine occur in sea salt, and the elements were isolated from material of this sort. On this account the family is known as the *halogen* family, and the elements as the *halogens*, these names signifying “producers of sea salt.” We have already made a partial study of chlorine and its hydride HCl (Chapter XV). In this chapter we shall study the other three elements and add something to our knowledge of the compounds of chlorine.

### FLUORINE

**Occurrence.** Fluorine occurs in nature most abundantly in the mineral *fluorite* ( $\text{CaF}_2$ ), in *cryolite* ( $\text{Na}_3\text{AlF}_6$ ), and in the complex mineral *fluorapatite* ( $3 \text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ ). Traces of compounds of fluorine are also found in many other minerals, in sea water, in bones, and in the enamel of the teeth.



**Properties of fluorine.** Fluorine is a gas, slightly yellow in color, and is 1.3 times as heavy as air. It can be obtained in the form of a yellow liquid which boils at  $-187^{\circ}$  and solidifies at  $-223^{\circ}$ .

**Preparation.** While the compounds of fluorine have been known for a long time, all attempts to isolate the free element resulted in failure until 1886, when the French chemist Moissan

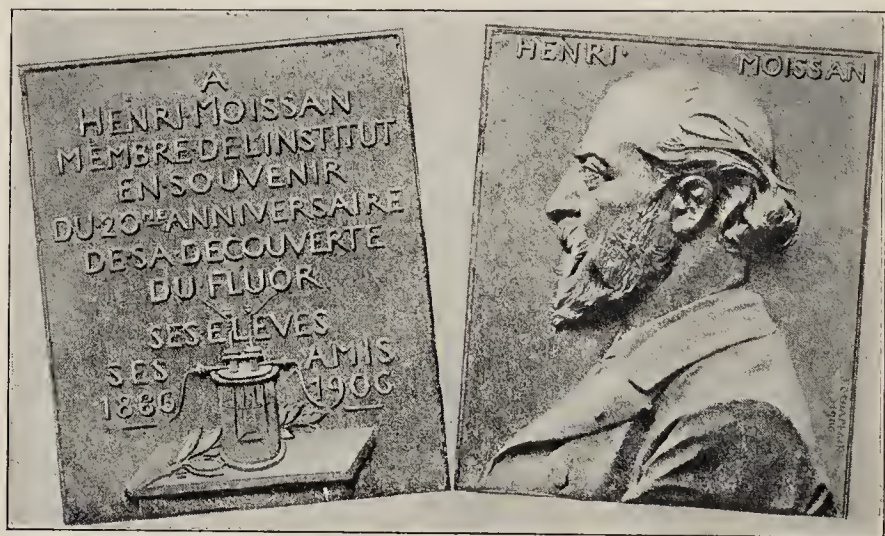
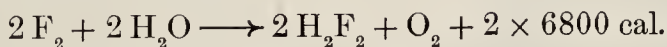


FIG. 120. Picture of tablet erected by the associates and friends of Moissan, in his laboratory in Paris, in 1906, on the twentieth anniversary of the isolation of fluorine

(Fig. 120) succeeded in obtaining it in a pure state. He prepared it by the electrolysis of hydrogen fluoride in which had been dissolved a little potassium hydrogen fluoride ( $\text{KHF}_2$ ) to render the liquid an electrolyte. The solution was placed in a U-shaped tube (Fig. 121) made of platinum (or copper), which was furnished with electrodes and exit tubes for the escape of the fluorine and hydrogen which are liberated, the former at the anode and the other at the cathode. Since hydrogen fluoride boils at  $19.4^{\circ}$ , the process must be carried out at a low temperature to prevent the liquid from vaporizing.

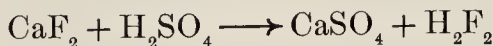
**Preparation from potassium hydrogen fluoride.** During the World War, experiments which were carried out under the direction of the United States government showed that fluorine can be prepared with comparative ease. It is only necessary to *melt* the solid potassium hydrogen fluoride ( $\text{KHF}_2$ ) in a copper vessel of suitable size, and subject the liquid salt to electrolysis.

**Chemical conduct.** Chemically fluorine is one of the most active of all elements. Most of the elements, when brought in contact with fluorine, combine with it with so much energy as to produce light. It unites with hydrogen with explosive violence and readily abstracts it from its compounds. For example, it decomposes water with great energy, forming hydrogen fluoride and oxygen :



It liberates all the other members of the chlorine family from their compounds with hydrogen and the metals. It does not combine with oxygen, however, and forms no oxygen acids. It attacks gold, platinum, and copper only superficially.

**Hydrogen fluoride ( $\text{H}_2\text{F}_2$ ).** Hydrogen fluoride is readily obtained from fluorite by the action of concentrated sulfuric acid, just as hydrogen chloride is obtained from sodium chloride (p. 184). The equation is as follows:



The formula is usually written  $\text{H}_2\text{F}_2$ , although by selecting the proper temperature the compound may be obtained in any of the forms indicated by the formulas  $\text{HF}$ ,  $\text{H}_2\text{F}_2$ ,  $\text{H}_3\text{F}_3$ . In its properties hydrogen fluoride resembles the hydrides of the other elements of this family, although it is more easily

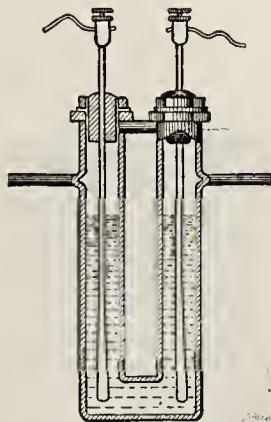


FIG. 121. Diagram of a metal U-tube for the preparation of fluorine

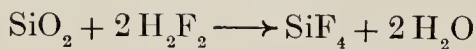
condensed to a liquid. It boils at  $19.4^{\circ}$  and can therefore be liquefied at ordinary pressures. It is soluble in all proportions in water. Its fumes are exceedingly irritating to the respiratory organs, and several chemists have lost their lives by accidentally breathing them.

**Hydrofluoric acid.** A solution of hydrogen fluoride in water is called *hydrofluoric acid*. Like other acids, it readily acts upon



FIG. 122. Picture of a bottle made out of ceresin, for holding hydrofluoric acid

bases and metallic oxides, and forms the corresponding salts called *fluorides*. It acts very vigorously upon organic matter, a single drop of the concentrated acid making a sore on the skin which is slow in healing and very painful. Its most characteristic property is its action upon silicon dioxide ( $\text{SiO}_2$ ), with which it forms water and the gas silicon tetrafluoride ( $\text{SiF}_4$ ), as shown in the equation



No other acid acts upon silicon in this way, and the reaction is very useful in chemical analysis.

Glass consists of certain compounds of silicon which are likewise acted on by the acid, so that it cannot be kept in glass bottles. It is preserved in leaden jugs or flasks made of a wax derived from petroleum and known as *ceresin* (Fig. 122). Ordinary commercial hydrofluoric acid contains about 50 per cent of hydrogen fluoride.

**Etching glass.** The action of hydrofluoric acid on silicon compounds is taken advantage of to etch designs upon glass. The glass is painted over with a protective paint upon which the acid will not act, the parts which it is desired to make opaque being left unprotected. A mixture of fluorite and sulfuric acid is then

painted over the vessel and after a few minutes is washed off. Wherever the hydrofluoric acid comes in contact with the glass it acts upon it, destroying its luster and making it opaque, so that the exposed design will be etched upon the clear glass. Frosted glass globes are often made in this way, but more frequently by a sand blast.

The etching may also be accomplished by covering the glass with a thin layer of paraffin, cutting the design through the wax, and then exposing the glass to the fumes of the gas.

## BROMINE

**History and occurrence.** Bromine was discovered in 1826 by the French chemist Ballard, who isolated it from sea salt. It occurs almost entirely in the form of sodium bromide ( $\text{NaBr}$ ) and magnesium bromide ( $\text{MgBr}_2$ ), which are found in many springs and salt deposits. The Stassfurt deposits in Germany and the salt waters of Michigan and Ohio are especially rich in bromides.

**Properties of bromine.** Bromine is a dark-red liquid whose density is 3.102. Its vapor has an offensive odor and is very irritating to the eyes and throat. The liquid boils at  $58.7^\circ$  and solidifies at  $-7.2^\circ$ , but even at ordinary temperatures it has a high vapor pressure, forming a reddish-brown gas very similar to nitrogen dioxide in appearance. 100 volumes of water dissolves about 1 volume of bromine at  $20^\circ$ , forming a reddish solution called *bromine water*. Bromine is much more readily soluble in carbon disulfide and in chloroform.

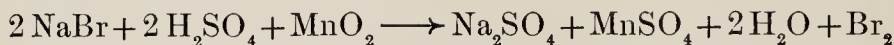
**Preparation of bromine.** The laboratory and the commercial method for preparing bromine are as follows:

1. **Laboratory method.** Just as chlorine is liberated by the action of hydrochloric acid on manganese dioxide (p. 175), so bromine may be liberated by a similar reaction, by using hydrobromic acid in place of hydrochloric. The equation for the reaction is as follows:





Hydrobromic acid is unstable and on this account is not usually available in the laboratory. It is therefore generated in the course of the reaction by using a mixture of sodium bromide and sulfuric acid. The equation for the complete reaction is as follows:



**Laboratory apparatus.** The materials are placed in a retort *A*, arranged as shown in Fig. 123. The end of the retort just touches the water in the flask *B*, which is partly immersed in ice water. As the contents of the retort are heated the bromine distills over and is collected in the cold receiver.

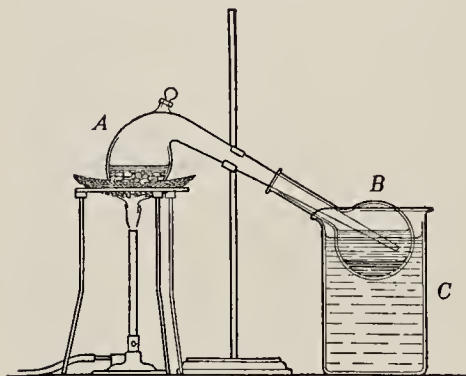
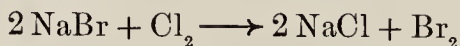


FIG. 123. Diagram of apparatus for the preparation of bromine in the laboratory

**2. Commercial method.** In the United States bromine is obtained commercially from salt water, the bromine being liberated by electrolysis. Some chlorine

is also set free in the process, but this reacts with the bromides present in the water; thus,



**Production.** Normally about 2,000,000 lb. of bromine is produced annually in the United States. By far the greatest amount of this comes from the salt waters near Midland, Michigan; the remainder comes from the salt waters of the Ohio River valley.

**Chemical conduct and uses.** In chemical conduct bromine is very similar to chlorine, except that it is less active. It combines directly with many of the same elements with which chlorine unites, but with less energy. It combines with hydrogen, and even abstracts it from some of its compounds. As would be expected, its bleaching action is much less



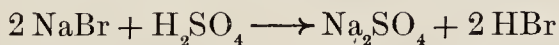
marked than that of chlorine. Its solution in water is used as an oxidizing agent but is not as effective as chlorine water.

Bromine is used chiefly in the preparation of bromides, which are employed to a considerable extent in photography and as medicinal agents. It is likewise used in the preparation of a number of organic drugs and dyestuffs.

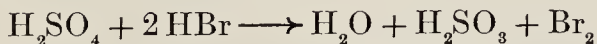
**Hydrogen bromide (HBr).** Hydrogen bromide is very similar to hydrogen chloride in its properties. It is a colorless gas and is very soluble in water, 1 volume of water dissolving 612 volumes of the gas under standard conditions. It differs from hydrogen chloride mainly in the fact that it is more unstable and consequently more readily oxidized.

The aqueous solution of hydrogen bromide is known as *hydrobromic acid*. This acid has properties similar to those of hydrochloric acid, but it is less stable. Even the oxygen of the air gradually acts upon it to form water and free bromine. It reacts with metals, their oxides, and their hydroxides to form bromides.

**Preparation of hydrogen bromide.** When sulfuric acid acts upon a bromide, hydrogen bromide is set free:

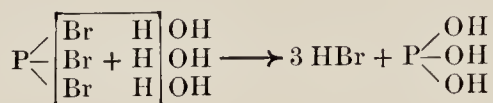


At the same time some bromine is liberated, as may be seen from the red fumes which appear, and from the odor. The explanation of this is found in the fact that hydrogen bromide is much *less stable* than hydrogen chloride and is therefore *more easily oxidized*. Concentrated sulfuric acid is a good oxidizing agent (p. 294) and oxidizes a part of the hydrogen bromide, liberating bromine:



The pure compound is best prepared by avoiding the presence of an oxidizing agent in its preparation. This can be accomplished by taking advantage of the action of water upon phosphorus tribromide, — a reaction in which hydrogen

bromide and phosphorous acid ( $\text{P}(\text{OH})_3$ , or  $\text{H}_3\text{PO}_3$ ) are formed. The reaction is made clearer by the use of structural formulas:



**Laboratory preparation.** The preparation of hydrogen bromide is conducted as follows: Red phosphorus, together with enough water to cover it, is placed in the flask *A* (Fig. 124), and bromine is put into the dropping funnel *B*. By means of the stopcock the bromine is allowed to flow drop by drop into the flask, the reaction taking place without the application of heat.

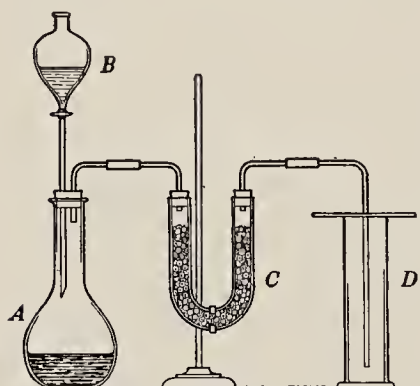


FIG. 124. Diagram of apparatus used in the preparation of hydrogen bromide in the laboratory

The phosphorus and bromine unite to form  $\text{PBr}_3$ , which then reacts with the water as expressed in the above equation. The U-tube *C* contains glass beads which have been moistened with water and rubbed in red phosphorus. Any bromine escaping action in the flask acts upon the phosphorus

in the U-tube. The hydrogen bromide is collected in *D* by displacement of air, or an aqueous solution of it may be prepared, as was done in the case of hydrogen chloride (Fig. 85).

## IODINE

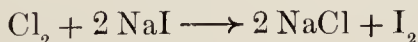
**History and occurrence.** Iodine is present in sea water, but in relatively small quantities. Certain seaweeds absorb the iodine from the water, in this way concentrating it within their tissues. It was from the ashes obtained by the burning of seaweed that the French chemist Courtois, in 1812, first isolated the element. Iodine is found in certain sponges, oysters, and fishes, but its chief source is from the deposits of Chile saltpeter

(sodium nitrate). It is interesting to note that small quantities of iodine exist in the thyroid gland of the human body.

**Properties.** Iodine is a purplish-black, shining solid which, when sublimed, crystallizes in brilliant plates. It has a density of 4.93, melts at  $113.5^{\circ}$ , and boils at  $184.3^{\circ}$ . The element has a strong, unpleasant odor, although the odor is not so disagreeable as that of chlorine or bromine. Even at ordinary temperatures it gives off a beautiful violet vapor, which increases in amount as heat is applied. It is only slightly soluble in water, 1 part being soluble in 3750 parts of water at  $15^{\circ}$ . It is very soluble in a solution of potassium iodide, forming a dark-brown solution. It also dissolves in carbon disulfide and in chloroform, forming a violet-colored solution.

**Preparation.** Iodine may be prepared in a number of ways, the principal methods being the following:

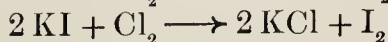
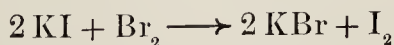
1. *Laboratory method.* Iodine can readily be prepared in the laboratory from an iodide by the method used in preparing bromine (Fig. 123), except that sodium iodide is substituted for sodium bromide. It can also be prepared by passing chlorine into a solution of an iodide:



2. *Commercial method.* Formerly iodine was obtained entirely from the ashes of seaweeds. While a small amount of the element is still obtained from this source, by far the largest supply comes from crude Chile saltpeter. It is present in these deposits in the form of sodium iodate ( $\text{NaIO}_3$ ) and is liberated by the action of the sulfites of sodium:



**Chemical conduct and uses.** Chemically iodine is quite similar to chlorine and bromine, but is still less active than bromine. Both chlorine and bromine displace it from its salts:



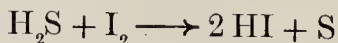
When even minute traces of iodine are added to thin starch paste a very intense blue color develops, and this reaction forms a delicate test for iodine. A solution of iodine in alcohol is called *tincture of iodine* and is extensively used in medicine. Iodine is also largely used in the preparation of iodides and of certain dyes and organic drugs. *Iodoform*, a common antiseptic, has the formula  $\text{CHI}_3$ . The supply of iodine is much larger than the demand. In normal times the United States uses about 500,000 lb. annually.

**Hydrogen iodide.** Hydrogen iodide resembles hydrogen chloride and hydrogen bromide in its physical properties, being a strongly fuming, colorless gas. It is 4.37 times as heavy as air. At  $10^\circ$  about 450 volumes of the gas dissolves in 1 volume of water.

**Preparation and conduct.** This compound is still less stable than hydrogen bromide; it follows, therefore, that it cannot be prepared by the action of sulfuric acid upon an iodide (p. 307). It is prepared by a method similar to that used in the preparation of hydrogen bromide; namely, by the action of phosphorus triiodide on water. Owing to the ease with which the gas is decomposed into its elements, it acts in many respects like nascent hydrogen, being a strong reducing agent. This might be expected from the fact that it is an endothermic compound, as shown in the equation



**Hydriodic acid.** The solution of hydrogen iodide in water has strong acid properties and is known as *hydriodic acid*. It is easily prepared by passing hydrogen sulfide into water in which finely divided iodine is suspended. The equation for the reaction is as follows:



The hydrogen iodide dissolves in the water as fast as formed, while the sulfur is precipitated and is removed by filtration.

**Chemical conduct of hydriodic acid.** Hydriodic acid differs from hydrochloric acid and hydrobromic acid mainly in the ease with which it is oxidized. The freshly prepared solution is colorless, but soon turns brown, owing to the liberation of iodine by the oxygen of the air:



As the action continues, the iodine separates in crystalline form. The acid, as well as hydrogen iodide, is therefore a strong reducing agent.

Hydriodic acid reacts with many of the metals, as well as with their oxides and hydroxides, to form the corresponding salts.

**Salts of hydrofluoric acid, hydrochloric acid, hydrobromic acid, and hydriodic acid : fluorides, chlorides, bromides, iodides.** Many of these salts are well-known compounds and have important uses. They can be prepared by the usual methods for preparing salts; namely, by the action of the acid upon the metals directly or upon their oxides or hydroxides. The most important fluoride is the well-known calcium fluoride ( $\text{CaF}_2$ ), or *fluorite*. The chlorides, bromides, and iodides resemble each other closely in their properties. They are all soluble in water except the silver, lead, and mercurous salts. Sodium chloride is the most important of the chlorides. Potassium bromide and potassium iodide are used in medicine, while silver bromide and iodide are largely used in photography.

## THE OXYGEN COMPOUNDS OF THE HALOGENS

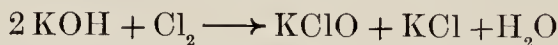
The halogens have but little affinity for oxygen, only chlorine and iodine forming oxides. While several oxygen acids are known, with few exceptions these are unstable and exist only in dilute solution. Both the acids and their salts readily give up oxygen. They are therefore good oxidizing agents and their chief use is for this purpose.



**The oxides.** Neither fluorine nor bromine form oxides, and, apart from the rare atmospheric gases, they are the only elements of which this is true. Chlorine forms three oxides: namely,  $\text{Cl}_2\text{O}$ ,  $\text{Cl}_2\text{O}_7$ , and  $\text{ClO}_2$ . They are difficult to prepare and very unstable. Iodine forms two oxides, of the formulas  $\text{I}_2\text{O}_4$  and  $\text{I}_2\text{O}_5$ . The latter, known as iodine pentoxide, is the best-known oxide of the group. It is a white solid and is fairly stable, but decomposes into iodine and oxygen when heated.

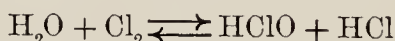
**The oxygen acids.** The most important of the oxygen acids of the halogens are the following:

1. **Hypochlorous acid ( $\text{HClO}$ ).** This acid is unstable and has been obtained only in dilute solutions. Its salts, known as the *hypochlorites*, may be prepared by passing chlorine into the *cold* solutions of the hydroxides of the metals. Thus, potassium hypochlorite ( $\text{KClO}$ ) is formed as indicated in the following equation:

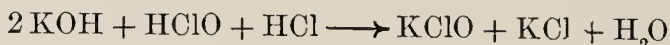


Both the acid and its salts easily give up their oxygen and are therefore good oxidizing agents.

**Details of the reaction.** It is probable that the chlorine first acts upon water (p. 180), forming hypochlorous and hydrochloric acids, thus:



The potassium hydroxide then neutralizes these acids as fast as they are formed, converting the equilibrium into a completed reaction (p. 245):



2. **Chloric acid ( $\text{HClO}_3$ ).** This acid is more stable than hypochlorous acid, but has not been obtained in a pure state. Its salts, the *chlorates*, may be prepared by passing chlorine into a *hot* solution of the hydroxides of the metals. Potassium chlorate, for example, is easily obtained by passing chlorine into a hot concentrated solution of potassium hydroxide:



It is probable that potassium hypochlorite forms first, as already explained. At the higher temperature this salt then decomposes as follows :



The chlorates are excellent oxidizing agents. Sodium chlorate and potassium chlorate are chiefly used in the preparation of explosives, fireworks, and oxygen.

**Preparation of hypochlorites and chlorates by electrolytic methods.** It will be recalled that the electrolysis of solutions of potassium chloride or of sodium chloride results in the formation of chlorine, together with the corresponding hydroxides of metals. It is possible so to regulate this process that the chlorine, instead of being evolved, is retained in the solution, together with the hydroxides, with which it acts to form hypochlorites or chlorates, according to the equations given above. This method is now coming into general use for the preparation of these salts. It is possible to obtain either the hypochlorites or the chlorates by properly choosing the conditions of the electrolysis.

3. *Perchloric acid* ( $\text{HClO}_4$ ). This acid is likewise unstable ; but it is possible to obtain it in a pure state, and a very concentrated solution may be had commercially. It is a colorless liquid and sometimes decomposes with great violence. Potassium perchlorate, the best known of its salts, is a white solid and, like the salts of other oxygen acids of chlorine, is an excellent oxidizing agent.

Hypobromous acid ( $\text{HBrO}$ ) and bromic acid ( $\text{HBrO}_3$ ), the analogues of hypochlorous acid and chloric acid, have also been prepared in dilute solution. The acids, as well as their salts, are similar to the corresponding chlorine compounds. Iodic acid ( $\text{HIO}_3$ ) and periodic acid ( $\text{H}_5\text{IO}_6$ ) are also known. They are both white solids. The acids, as well as their salts, are strong oxidizing agents.

## PERIODIC RELATIONS OF THE HALOGEN ELEMENTS

A review of the properties of the four halogen elements, and a comparison of their compounds, will show the relations that we expect among the members of a periodic family.

1. The first element (fluorine) stands somewhat apart from the others, while the latter have a close periodic relation. We shall find that this is a general rule in all families. Thus, oxygen stands apart from the other members in its family.

2. The physical constants of the elements vary somewhat regularly as we pass from element to element, as may be seen in the table at the head of this chapter.

3. The *type* of compound as shown in the formulas is much the same for all the elements, as is shown in the table, though not all the elements form all the corresponding compounds.

HYDRIDES	OXIDES	OXYGEN ACIDS
H <sub>2</sub> F <sub>2</sub>	—	—
HCl	Cl <sub>2</sub> O, Cl <sub>2</sub> O <sub>7</sub> , ClO <sub>2</sub>	HClO, HClO <sub>2</sub> , HClO <sub>3</sub> , HClO <sub>4</sub>
HBr	—	HBrO, HBrO <sub>2</sub> , HBrO <sub>3</sub>
HI	I <sub>2</sub> O <sub>4</sub> , I <sub>2</sub> O <sub>5</sub>	HIO, HIO <sub>2</sub> , HIO <sub>3</sub> , H <sub>5</sub> IO <sub>6</sub>

4. The characteristics in any one series of compounds vary rather regularly as we pass from compound to compound. This is shown in the table:

Hydrogen fluoride (H<sub>2</sub>F<sub>2</sub>): a stable liquid boiling at 19.4°.

Hydrogen chloride (HCl): a stable gas liquefying at - 85°.

Hydrogen bromide (HBr): an unstable gas liquefying at - 67°.

Hydrogen iodide (HI): a very unstable gas liquefying at - 35.5°.

## EXERCISES

1. How do we account for the fact that liquid hydrogen fluoride does not conduct the electric current?

2. Why is sulfuric acid used for liberating hydrogen fluoride from fluorite?

3. Why is the formula for hydrogen fluoride written H<sub>2</sub>F<sub>2</sub>, while that of hydrogen chloride is written HCl?

4. What discoveries made by Moissan have been noted other than the preparation of fluorine?

5.  $\text{Cl}_2\text{O}$  is the anhydride of what acid?

6. A solution of hydrogen iodide turns brown on standing. How is this accounted for?

7. How can bromine vapor be distinguished from nitrogen dioxide?

8. Write the equations for the reaction which takes place when hydrogen iodide is prepared from iodine, phosphorus, and water.

9. Judging from their behavior toward sulfuric acid, to what class of agents do hydrobromic acid and hydriodic acid belong?

10. Give the derivation of the names of the elements of the chlorine family.

11. Write the names and formulas for the binary acids of the chlorine group in the order of the stability of the acids.

12. What is formed when a metal dissolves in each of the following: nitric acid; dilute sulfuric acid; concentrated sulfuric acid; hydrochloric acid; aqua regia?

13. How could you distinguish between a chloride, a bromide, and an iodide?

14. In what respects are the elements included in the chlorine family similar?

15. What substances so far studied are used as bleaching agents? To what is the bleaching action of each due?

16. What weight of sodium chloride is necessary to prepare sufficient hydrogen chloride to saturate 1 liter of water under standard conditions?

17. What weight of fluorite is necessary for the preparation of 1 kg. of the commercial hydrofluoric acid?

18. The concentrated hydrochloric acid of commerce has a density of 1.20 and contains 40 per cent of hydrogen chloride. What weights of salt and sulfuric acid are necessary to prepare 100 kg. of this acid?

19. A certain salt water has a density of 1.22 and contains 0.12 per cent of bromine. What volume of this water would be required in the preparation of 10 kg. of bromine?

20. What weights of chlorine and potassium hydroxide are necessary for the preparation of 1 kg. of potassium chlorate? Does this process appeal to you as an economical method of preparation?

21. On decomposition 100 liters of hydrogen chloride would yield how many liters of hydrogen and of chlorine?

## CHAPTER XXIV

### THE PHOSPHORUS FAMILY

NAME OF ELEMENT	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT
Phosphorus . . . . .	P	31.02	1.82	44.1°
Arsenic . . . . .	As	74.96	5.7	sublimes
Antimony . . . . .	Sb	121.77	6.68	630.5°
Bismuth . . . . .	Bi	209.00	9.8	271°

**The family.** The elements constituting this family belong in the same group with nitrogen and therefore resemble it in a general way in the type of compounds formed. They differ from nitrogen much as the other halogen elements differ from fluorine, or the members of the sulfur family from oxygen. They exhibit the gradation of physical properties shown in the above table. The same general gradation is also found in their chemical characteristics, phosphorus being an acid-forming element, while bismuth is essentially a metal. The other two elements are intermediate in character.

### PHOSPHORUS

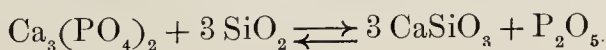
**History.** The element phosphorus was discovered by the alchemist Brand, of Hamburg, in 1669, while he was searching for the philosophers' stone. Owing to its peculiar properties and the secrecy which was maintained about its preparation it remained a very rare and costly substance until the demand for it in the manufacture of matches brought about its production on a large scale.



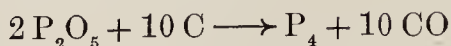
**Properties.** The usual form of phosphorus, called *white*, or *yellow, phosphorus*, is a nearly colorless, translucent, waxy solid which melts at  $44.1^{\circ}$  and boils at  $280^{\circ}$ . It can therefore be cast into any convenient form under warm water, and is usually sold on the market in the form of sticks. It can be cut with a knife, but this must always be done under water, since phosphorus is extremely inflammable and the friction of the knife blade is almost sure to set it on fire if it is cut in the air. It is not soluble in water but is freely soluble in some other liquids, notably in carbon disulfide. Its density is 1.8. One gram-molecular volume (22.4 liters) of phosphorus vapor weighs about 128 g., which is approximately four times the atomic weight, showing that the formula of the molecule is  $P_4$ .

**Occurrence.** Owing to its great chemical activity phosphorus never occurs free in nature. In the form of phosphates it is very abundant and widely distributed. *Phosphorite* is the chief mineral form of calcium phosphate, while *apatite* consists of calcium phosphate together with calcium fluoride or calcium chloride. These minerals form very large deposits and are extensively mined for use as fertilizers. Calcium phosphate is a constituent of all fertile soil, having been supplied to the soil by the disintegration of rocks containing it. It is the chief mineral constituent of the bones of animals, and bone ash is therefore nearly pure calcium phosphate.

**Preparation.** Phosphorus is now manufactured from bone ash or a pure mineral phosphate by heating the phosphate with sand and carbon in an electric furnace. Sand consists largely of silica ( $SiO_2$ ), and this is the anhydride of metasilicic acid ( $H_2SiO_3$ ). At very high temperatures phosphoric anhydride ( $P_2O_5$ ) is volatile, while at the same temperature silica is not. Consequently when calcium phosphate is heated with silica the following equilibrium is set up:



The phosphoric anhydride formed in the reaction is then reduced by the carbon as follows:



**Apparatus.** The materials are fed in at *A* (Fig. 125) by the feed screw *B*. The phosphorus vapor escapes at *D* and is condensed under water, while the calcium silicate is tapped off as a liquid at *C*. The phosphorus obtained in this way is quite impure and is purified by distillation or by melting it and pressing it through cloth.

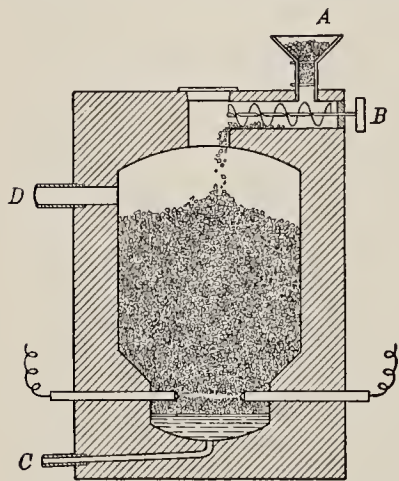


FIG. 125. Diagram showing the general construction of a furnace used for the production of phosphorus

**Chemical conduct.** When exposed to the air phosphorus slowly combines with oxygen, and in so doing gives out a pale light, or *phosphorescence*, which can be seen only in a dark place. The heat of the room may raise the temperature of phosphorus to the kindling point, when it burns with a sputtering flame, giving off

dense fumes of oxide of phosphorus. It burns with dazzling brilliancy in oxygen and combines directly with many other elements. On account of its great attraction for oxygen it is preserved under water.

Phosphorus is very poisonous, from 0.2 to 0.3 g. being a fatal dose.

**Uses.** White phosphorus is used in making pure phosphoric acid, and for minor purposes in chemical laboratories. During the World War large quantities were used in generating smoke clouds ( $\text{P}_2\text{O}_5$ ) for concealing troops and ships (Fig. 126). The incendiary bullets which proved so disastrous to the Zeppelins during the war contained free phosphorus. When

fired the phosphorus was ignited by the friction of the air, and, on hitting a balloon or Zeppelin, set fire to the hydrogen with which it was filled. *The chief use of phosphorus, however, is in the making of matches.*

**Red phosphorus.** On standing, white phosphorus gradually undergoes a remarkable change, being converted into a dark-red powder which has a density varying from 2.1 to 2.38.



FIG. 126. Picture illustrating the use of phosphorus in the World War for the production of smoke clouds to conceal troops

This form of phosphorus is called *red phosphorus*. It no longer takes fire easily; it is not soluble in carbon disulfide; it is not poisonous, — in fact, it is an entirely different substance.

The velocity of this change of white phosphorus to red phosphorus increases with rise in temperature, and red phosphorus is therefore prepared by heating the white form a little below the boiling point. When distilled and quickly condensed, the red form changes back to the white. This is in accordance with the general rule that *when a substance capable of existing*

*in several forms is condensed from a gas or crystallized from the liquid state, the more unstable variety forms first, and this then passes into the more stable forms.*

In addition to white and red phosphorus, several other allotropic forms are known.

**Matches.** Friction matches containing phosphorus first came into use in 1827, and at present two general varieties are in common use. The more common variety, which will ignite when rubbed against any rough surface, is made by dipping the match stick first into some inflammable substance, such as melted paraffin, and afterwards into a paste consisting of (1) phosphorus sesquisulfide,  $P_4S_3$ ; (2) some oxidizing substance, such as manganese dioxide, red lead, or potassium chlorate; and (3) a binding material, such as glue or dextrin. On friction the phosphorus is ignited, the combustion being supported by the oxidizing agent and communicated to the wood by the burning paraffin. In sulfur matches the paraffin is replaced by sulfur.

In the *safety* match red phosphorus, an oxidizing agent, and some gritty material, such as powdered glass, are mixed with glue and placed on the side of the box. The match tip is provided with an oxidizing agent and an easily combustible substance, usually antimony sulfide. The match cannot easily be ignited by friction except on the prepared surface.

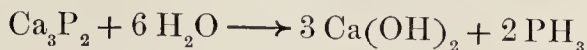
Constant working with white phosphorus frequently results in dreadful diseases of the bones of the face, while many disastrous fires are caused by accidental ignition of matches containing it. On this account the manufacture and use of such matches is prohibited by law in many countries. The Congress of the United States in 1913 accomplished the same end by imposing a prohibitive tax upon white-phosphorus matches.

**Hydrides of phosphorus — phosphine ( $PH_3$ ).** Phosphorus forms several compounds with hydrogen, the best known of which is *phosphine* ( $PH_3$ ), analogous to ammonia ( $NH_3$ ).

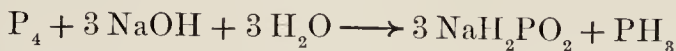
Phosphine is a gas of unpleasant odor and is exceedingly poisonous. Like ammonia, it forms salts with the halogen acids. Thus, we have *phosphonium chloride* ( $PH_4Cl$ ), analogous to ammonium chloride ( $NH_4Cl$ ).



**Preparation of phosphine.** The simplest way of making phosphine is to treat calcium phosphide with water:



It is more conveniently made by boiling white phosphorus suspended in a concentrated solution of sodium hydroxide, the reaction being a complicated one:



**Laboratory preparation.** Phosphine can be conveniently made in the apparatus shown in Fig 127. A concentrated solution of sodium hydroxide, together with several small bits of phosphorus, are placed in the flask *A*, and (to remove oxygen) a current of coal gas is passed into the flask through the tube *B* until all the air has been displaced. The gas is then turned off and the flask is heated. Phosphine is formed in small quantities and escapes through the delivery tube, the exit of which is just covered by the water in the vessel *C*. Each bubble of the gas as it escapes into the air takes fire, and the product of the combustion ( $\text{P}_2\text{O}_5$ ) forms beautiful rings, which float unbroken for a considerable time in quiet air. The pure phosphine does not take fire spontaneously. When prepared as directed above, a second hydride of phosphorus ( $\text{P}_2\text{H}_4$ ) is present which imparts this property.

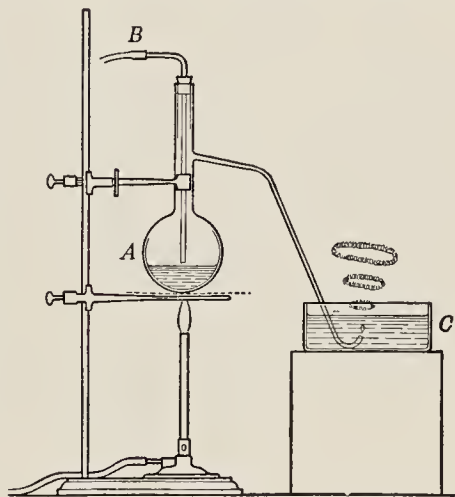


FIG. 127. Diagram of apparatus used in the preparation of phosphine

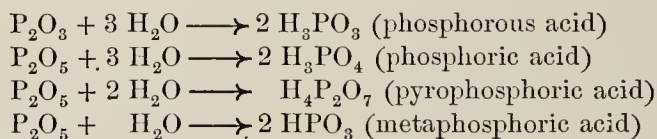
**Oxides of phosphorus.** Phosphorus forms two well-known oxides: the trioxide ( $\text{P}_2\text{O}_3$ ) and the pentoxide ( $\text{P}_2\text{O}_5$ ), sometimes called phosphoric anhydride. When phosphorus burns in an insufficient supply of air the product is partially the trioxide; in oxygen or an excess of air, the pentoxide, which is



much the better known of the two. It is a snow-white, voluminous powder whose most marked property is its great affinity for water. It has no chemical action upon most gases, so that they can be thoroughly dried by allowing them to pass through properly arranged vessels containing phosphorus pentoxide.

**Chlorides of phosphorus.** Phosphorus burns readily in chlorine and forms the liquid *trichloride* ( $\text{PCl}_3$ ) or the solid *pentachloride* ( $\text{PCl}_5$ ) according to the amount of chlorine available. Both these compounds have important uses in the preparation of many organic compounds.

**Acids of phosphorus.** In combination with oxygen and hydrogen, phosphorus forms a large number of acids. The most important of these are derived from the anhydrides  $\text{P}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ . The names of these acids and their relations to the anhydrides are as follows:

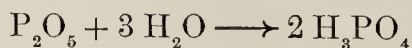


**Phosphorous acid ( $\text{H}_3\text{PO}_3$ ).** Neither phosphorous acid nor its salts (the phosphites) are at all frequently met with in chemical operations. It can be easily obtained, however, in the form of transparent crystals when phosphorus trichloride is treated with water and the resulting solution evaporated:



It is a powerful reducing agent because of its tendency to take up oxygen and pass over into phosphoric acid.

**Phosphoric acid (orthophosphoric acid) ( $\text{H}_3\text{PO}_4$ ).** This acid can be obtained by dissolving phosphorus pentoxide in boiling water, as represented in the equation



It is usually made by treating calcium phosphate with concentrated sulfuric acid. The calcium sulfate produced in the reaction is nearly insoluble and can be filtered off, leaving

the phosphoric acid in solution. Very pure acid is made by oxidizing phosphorus with nitric acid. It forms large, colorless crystals which are exceedingly soluble in water.

**Phosphates (orthophosphates).** Since phosphoric acid is a *tribasic* acid, it forms acid salts as well as normal salts. Thus the following sodium phosphates are known :

$\text{NaH}_2\text{PO}_4$	. . . . .	sodium dihydrogen phosphate
$\text{Na}_2\text{HPO}_4$	. . . . .	disodium hydrogen phosphate
$\text{Na}_3\text{PO}_4$	. . . . .	normal sodium phosphate



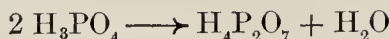
FIG. 128. View of a rock phosphate quarry in Florida

Phosphoric acid also forms *mixed* salts ; that is, salts containing two different metals. The most familiar compound of this kind is sodium ammonium acid phosphate (*microcosmic salt*), which has the formula  $\text{Na}(\text{NH}_4)\text{HPO}_4$ .

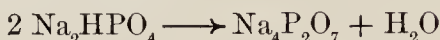
The phosphates constitute an important class of salts. The normal salts are nearly all insoluble and many of them occur in nature. The monohydrogen phosphates are as a rule insoluble, while most of the dihydrogen salts are soluble.

The rock phosphates of Florida and Tennessee contain about 70 per cent of calcium phosphate  $\text{Ca}_3(\text{PO}_4)_2$ . They are mined in large quantities and used in making fertilizers (Fig. 128).

**Pyrophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_7$ ).** On heating phosphoric acid to about  $225^\circ$ , pyrophosphoric acid is formed in accordance with the following equation:



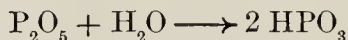
It is a white crystalline solid. Its salts can be prepared by heating a monohydrogen phosphate:



**Metaphosphoric acid (glacial phosphoric acid) ( $\text{HPO}_3$ ).** This acid is formed when phosphoric acid is heated above  $400^\circ$ :

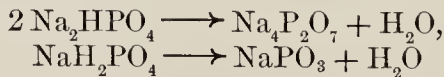


It is also formed when phosphorus pentoxide is treated with cold water:



It is a white crystalline solid and is so stable toward heat that it can be fused and even volatilized without decomposition. On cooling from the fused state it forms a glassy solid, and on this account is often called *glacial* phosphoric acid. It possesses the property of dissolving small quantities of metallic oxides, with the formation of compounds which, in the case of certain metals, have characteristic colors. It is therefore used in the detection of these metals.

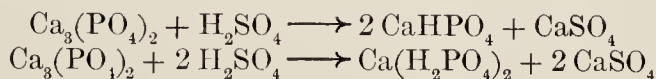
While the monohydrogen phosphates, on heating, give salts of pyrophosphoric acid, the dihydrogen phosphates yield salts of metaphosphoric acid. The equations representing these reactions are as follows:



**Hypophosphorous acid ( $\text{H}_3\text{PO}_2$ ).** A fifth acid of phosphorus, known as hypophosphorous acid, is well known, and its salts find a wide use in medicine.

**Sulfides of phosphorus.** A number of compounds consisting of phosphorus and sulfur can be obtained by heating the two elements in various proportions. The most important of these has the formula  $\text{P}_4\text{S}_3$  and is called *phosphorus sesquisulfide*. As we have seen, it is an important component in the manufacture of matches.

**Phosphate fertilizers.** Phosphorus is essential to the growth of both vegetable and animal organisms, and consequently its compounds must be present in every fertile soil. Since these compounds are never abundant, and crops containing phosphorus are constantly removed from the land, the supply must be renewed in some way. The large mineral deposits of rock phosphates are the only source from which a supply can be obtained, and these deposits are confined to rather limited localities. The pulverized rock is sometimes applied directly, but it is too insoluble to be absorbed easily by plants, and hard to spread evenly through the soil. It is usually first treated with sulfuric acid, to secure one or both of the following reactions :



Calcium dihydrogen phosphate ( $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ) is freely soluble in water, and calcium hydrogen phosphate ( $\text{CaHPO}_4$ ), while insoluble in water, is soluble in weak acids such as are always present about the roots of growing plants. This treatment also adds sulfur to the soil as calcium sulfate, and this is often very beneficial, since plants need sulfur as well as phosphorus.

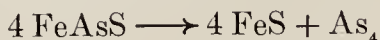
## ARSENIC

**Occurrence.** Arsenic occurs in considerable quantities in nature as the native element, as the sulfides *realgar* ( $\text{As}_2\text{S}_2$ ) and *orpiment* ( $\text{As}_2\text{S}_3$ ), as oxide ( $\text{As}_2\text{O}_3$ ), and as a constituent of many metallic sulfides, such as *arsenopyrite* ( $\text{FeAsS}$ ), often called *mispickel*.

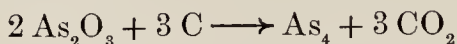
**Properties.** Arsenic is a steel-gray, metallic-looking substance of density 5.72. Like phosphorus, its molecules contain four atoms ( $\text{As}_4$ ). Though resembling metals in appearance, it is quite brittle, being easily powdered in a mortar. When strongly heated it sublimes; that is, it passes into a vapor without melting, and condenses again to a crystalline solid when the vapor is cooled. Like phosphorus it can be obtained in several allotropic forms.



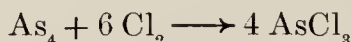
**Preparation.** The element is prepared by purifying the native arsenic or by heating the arsenopyrite in iron tubes, out of contact with air. In the latter case the reaction is expressed by the following equation:



The arsenic, being volatile, condenses in chambers connected with the heated tubes. It is also made from the oxide by reduction with carbon:



**Conduct and uses.** Arsenic alloys readily with some of the metals and finds its chief use as an alloy with lead which is used for making shot, the alloy being harder than pure lead and forming rounder drops (shot). When heated on charcoal with the blowpipe, arsenic is converted into an oxide which volatilizes, leaving the charcoal unstained by any oxide coating. It burns readily in chlorine gas, forming arsenic trichloride:

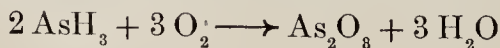


It is not a very active element and, unlike most of its compounds, is not itself poisonous.

**Arsine ( $\text{AsH}_3$ ).** When any compound containing arsenic is brought into the presence of nascent hydrogen, *arsine* ( $\text{AsH}_3$ ), corresponding to phosphine and ammonia, is formed. The reaction when oxide of arsenic is so treated is

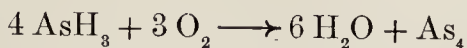


Arsine is a gas with a peculiar garlic-like odor and is intensely poisonous. A single bubble of the pure gas has been known to prove fatal. It is an unstable compound, decomposing into its elements when heated to a moderate temperature. It is combustible and burns with a pale, bluish-white flame to form arsenic trioxide and water when air is in excess:





When the supply of air is deficient, water and metallic arsenic are formed:



These reactions make the detection of even minute quantities of arsenic a very easy problem.

**Marsh's test for arsenic.** The method devised by Marsh for detecting arsenic is frequently used and illustrates the formation and properties of arsine. The apparatus is shown in Fig. 129.

Hydrogen is generated in the flask *A* by the action of dilute sulfuric acid on zinc, is dried by being passed over calcium chloride in the tube *B*, and, after passing through the hard-glass tube *C*, is ignited at the jet *D*. If a substance containing arsenic is now introduced into the

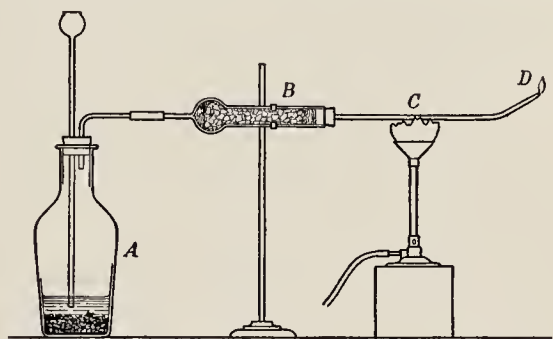


FIG. 129. Marsh's apparatus for the detection of arsenic

generator *A*, the arsenic is converted into arsine by the action of the nascent hydrogen and passes to the jet along with the hydrogen. If the tube *C* is strongly heated at some point near the middle, the arsine is decomposed while passing this point, and the arsenic is deposited just beyond the heated point in the form of a shining, brownish-black mirror. A small fraction of a milligram of arsenic can be detected by this test. If the tube is not heated, the arsine burns along with the hydrogen at the jet. Under these conditions a small porcelain dish crowded down into the flame is blackened by a spot of metallic arsenic, for the arsine is decomposed by the heat of the flame, and the arsenic, cooled below its kindling temperature by the cold porcelain, deposits upon it as a black spot.

**Oxides of arsenic.** Arsenic forms two oxides,  $\text{As}_2\text{O}_3$  and  $\text{As}_2\text{O}_5$ , corresponding to the oxides of phosphorus. Of these the white crystalline powder, *arsenious oxide*, or arsenic trioxide ( $\text{As}_2\text{O}_3$ ), is much the better known and is the substance usually

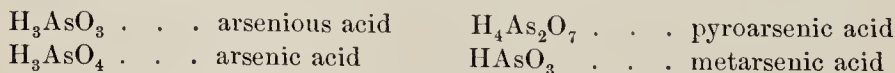
called *white arsenic*, or merely arsenic. It is found as a mineral but is more often obtained as a by-product in various industries in which metallic sulfides are burned in air, especially from the copper smelters of Montana. The sulfides contain small quantities of arsenic, and when they are burned arsenious oxide is formed as a vapor, together with sulfur dioxide:



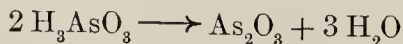
The arsenious oxide is condensed in appropriate chambers. It is obtained either as a white crystalline powder or in large, vitreous lumps resembling lumps of porcelain in appearance.

**Conduct and uses.** Arsenious oxide has no basic properties, and we have no salts such as arsenic sulfate. It is the anhydride of arsenious acid. It is extremely poisonous, from 0.2 to 0.3 g. being a fatal dose. It is frequently given as a poison, since it is nearly tasteless and does not act rapidly. This slow action is due to the fact that it is not very soluble and hence is absorbed slowly by the system. Arsenious oxide is also used as a chemical reagent in glassmaking, in the dye industry, and in the manufacture of arsenical pigments and insecticides. A number of complex organic compounds containing arsenic are used in medicine, especially in the treatment of diseases due to microorganisms. The best-known of these is the complex compound known as *Salvarsan*.

**Acids of arsenic.** Like the corresponding oxides of phosphorus, the oxides of arsenic are acid anhydrides. In solution they combine with bases to form salts corresponding to the salts of the acids of phosphorus. Thus, we have salts of the following acids:

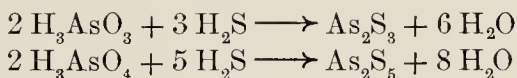


Several other acids of arsenic are also known. Not all of these can be obtained as free acids, since they tend to lose water and form the oxides. Thus, instead of obtaining arsenious acid ( $\text{H}_3\text{AsO}_3$ ), the oxide  $\text{As}_2\text{O}_3$  is obtained:



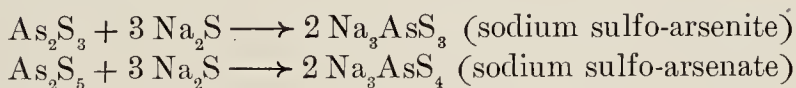
Salts of all the acids are known, however, and some of them have commercial value. Most of them are insoluble, and some of the copper salts, which are green, are used as pigments. Paris green, which has a complicated formula, is a well-known insecticide. Lead arsenate, whose formula is somewhat variable, but which is largely the arsenate  $\text{Pb}_3(\text{AsO}_4)_2$ , is extensively used as a spray on fruit trees. Calcium arsenate is widely used in combating the boll weevil in the cotton fields of the South.

**Sulfides of arsenic.** When hydrogen sulfide is passed into an acidified solution containing an arsenic compound, the arsenic is precipitated as a bright-yellow sulfide, thus:



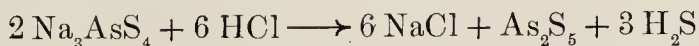
In this respect arsenic resembles the metallic elements, many of which produce sulfides under similar conditions. The sulfides of arsenic, both those produced artificially and those found in nature, are used as yellow pigments.

**Sulfo-salts of arsenic.** When either the trisulfide ( $\text{As}_2\text{S}_3$ ) or the pentasulfide ( $\text{As}_2\text{S}_5$ ) is treated with a solution of a *soluble sulfide*, such as sodium sulfide ( $\text{Na}_2\text{S}$ ), it is dissolved; and when the solution is evaporated, well-crystallized *sulfo-salts* are obtained:



It will be noticed that these sulfo-salts differ from the arsenite and the arsenate in that *the oxygen of the latter has been replaced by sulfur*.

When a solution of a sulfo-salt is treated with hydrochloric acid, the original sulfide is precipitated:



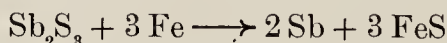
Three of the common elements (arsenic, antimony, and tin) form sulfo-salts of this kind, and by taking advantage of the reactions just described these elements may be separated from all others in chemical analysis.

## ANTIMONY

**Properties.** Antimony is a bluish-white, metallic-looking substance whose density is 6.68. It is highly crystalline, hard, and very brittle. It has a rather low melting point ( $630.5^{\circ}$ ) and expands noticeably on solidifying.

**Occurrence.** Antimony occurs in nature chiefly as the sulfide ( $\text{Sb}_2\text{S}_3$ ), called *stibnite*, though it is also found as the oxide and as a constituent of many complex minerals. Most of the commercial supply of the element comes from China and Japan.

**Preparation.** Antimony is prepared from the sulfide in a very simple manner. The sulfide is melted with scrap iron in a furnace, when the iron combines with the sulfur to form a liquid layer of melted iron sulfide, while the heavier liquid, antimony, settles to the bottom and is drawn off from time to time. The reaction involved is represented by the equation



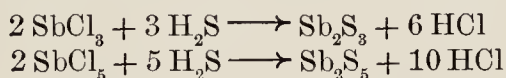
**Chemical conduct.** In chemical properties antimony resembles arsenic in many particulars. It forms the oxides  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$ , and in addition  $\text{Sb}_2\text{O}_4$ . It combines with the halogen elements with great energy, burning brilliantly in chlorine to form antimony trichloride ( $\text{SbCl}_3$ ). When heated on charcoal with the blowpipe it is oxidized and forms on the charcoal a coating of antimony oxide which has a characteristic bluish-white color.

**Stibine ( $\text{SbH}_3$ ).** The gas stibine ( $\text{SbH}_3$ ) is formed under conditions which are very similar to those which produce arsine, and it closely resembles the latter compound, though it is still less stable. It is very poisonous.

In Marsh's test for arsenic any antimony that is present is converted into stibine, and this results in a black mirror deposit, as in the case of arsenic. The deposit is more sooty in appearance than is the arsenic deposit, and it is not dissolved by a solution of sodium hypochlorite, whereas the deposited arsenic is dissolved by this reagent.

**Acids of antimony.** The oxides  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$  are weak acid anhydrides and are capable of forming two series of acids corresponding in formulas to the acids of phosphorus and arsenic. They are much weaker, however, and are of little practical importance.

**Sulfides of antimony.** Antimony resembles arsenic in that hydrogen sulfide precipitates it as a sulfide when the hydrogen sulfide is conducted into an acid solution containing an antimony compound:



The two sulfides of antimony are called the trisulfide and the pentasulfide respectively. When prepared in this way they are orange-colored substances, though the mineral stibnite is black. The sulfides of antimony are used in the manufacture of matches and of red rubber.

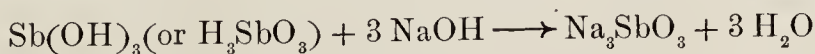
**Sulfo-salts of antimony.** Like the sulfides of arsenic, the sulfides of antimony dissolve in solutions of soluble sulfides and form the corresponding sulfo-salts. Of these the best known are *sodium sulfo-antimonite* ( $\text{Na}_3\text{SbS}_3$ ) and *sodium sulfo-antimonate* ( $\text{Na}_3\text{SbS}_4$ ).

**Metallic properties of antimony.** The physical properties of the element are those of a metal, and the fact that its sulfide is precipitated by hydrogen sulfide shows that it acts like a metal in a chemical way. Its hydroxide ( $\text{Sb}(\text{OH})_3$ ) dissolves in acids, forming salts, and in such reactions acts as a base:



Many other reactions show that antimony has more of the properties of a metal than of a nonmetal.

**Amphoteric hydroxides.** While antimony hydroxide has undoubted basic properties, *it also acts as a weak acid*; thus,

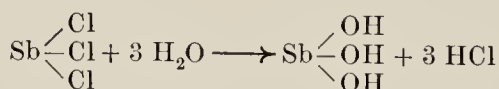


*A hydroxide that can act either as a base or as an acid is called an amphoteric hydroxide.* As we might expect, an amphoteric hydroxide is always very weak both as an acid and as a base.

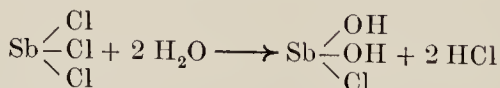


**Oxygen acids really hydroxides.** It may appear a little inconsistent to think of an acid as a *hydroxide*, but in reality nearly all oxygen acids, as well as all bases, are hydroxyl compounds. Thus, sulfuric acid is  $\text{SO}_2(\text{OH})_2$  (p. 291). The real distinction between an acid and a base is not a question of the possession of hydroxyl groups, but of *the way the compound ionizes*. If a hydroxyl compound gives hydrogen ions, it is an acid; if it gives hydroxyl ions, it is a base; if some molecules of a compound ionize one way and some the other, giving both hydrogen ions and hydroxyl ions, it is an *amphoteric hydroxide*. As a rule, metallic hydroxides are bases, while the hydroxides of nonmetals are acids.

**Hydrolysis of antimony salts.** Since antimony hydroxide ( $\text{Sb}(\text{OH})_3$ ) is a very *weak* base, we should expect its salts to be decomposed, or hydrolyzed, by water (p. 246). If antimony chloride were to be *completely* hydrolyzed, the equation would be as follows:



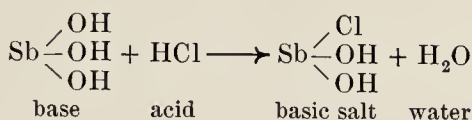
The reaction is not so complete, however, only two of the three chlorine ions being replaced by hydroxyl ions:



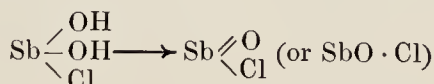
If we wish to prevent this hydrolysis, we must add hydrochloric acid in sufficient quantity to reverse the reaction of hydrolysis by mass action (p. 240).

**Basic salts and oxysalts.** The compound formed by the partial hydrolysis of antimony chloride is unlike any we have yet met. Since it contains hydroxyl radicals combined with a metal, we must regard it as a *base*; but it also contains a chlorine atom combined with a metal, so that it is likewise

a *salt*. Since it has the characteristics of both a base and a salt, it is a *basic salt* (p. 200).



The basic chloride of antimony easily loses water, as shown in the equation



The resulting compound is at once both an oxide and a salt, and such compounds are called *oxysalts*. This particular compound is called antimony oxychloride.

## BISMUTH

**Properties.** Bismuth is a heavy, crystalline, brittle metal nearly the color of silver, but with a slightly rosy tint which distinguishes it from other metals. It melts at a low temperature (271°) and has a density of 9.8. It is not acted upon by the air at ordinary temperatures.

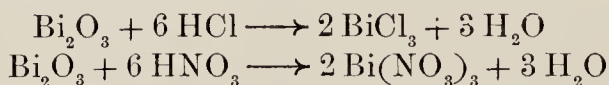
**Occurrence.** Bismuth is usually found in the uncombined form in nature. It also occurs as oxide and sulfide and as a constituent of many rare minerals. Most of the bismuth of commerce comes from Bolivia. Smaller quantities are produced in parts of Europe, Australia, and Colorado. It is not an abundant element.

**Preparation.** Bismuth is prepared by merely heating the ore containing the native bismuth and allowing the metal to run out into suitable vessels. Other ores are converted into oxides and reduced by heating with carbon. It is difficult to prepare the metal in a high state of purity.

**Chemical conduct.** When heated with the blowpipe on charcoal, bismuth gives a coating of the oxide  $\text{Bi}_2\text{O}_3$ . This has a yellowish-brown color which easily distinguishes it from

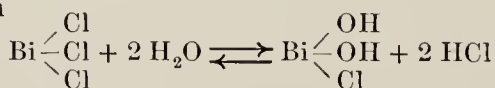
the oxides formed by other metals. It combines very readily with the halogen elements, powdered bismuth burning readily in chlorine. It is below hydrogen in the electrochemical series (p. 216), and in the absence of air it is not acted upon by hydrochloric acid. It is readily attacked by oxidizing acids such as nitric acid.

**Compounds of bismuth.** Unlike the other elements of this group, bismuth has almost no acid properties. Its chief oxide,  $\text{Bi}_2\text{O}_3$ , is basic in its properties. It dissolves in strong acids and forms salts of bismuth:



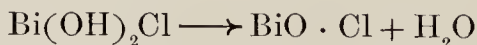
The nitrate and the chloride of bismuth can be obtained as well-formed, colorless crystals.

Bismuth hydroxide is a weak base, and its salts, like those derived from antimony hydroxide, undergo partial hydrolysis in dilute solution. Thus, bismuth chloride is hydrolyzed according to the equation



This action is reversible, and by adding excess of hydrochloric acid the basic chloride is changed into the normal chloride.

By loss of water the basic chloride is converted into bismuth oxychloride:



In a similar way bismuth nitrate forms the compound  $\text{BiO} \cdot \text{NO}_3$ , known as bismuth oxynitrate or subnitrate.

## ALLOYS

**Nature of alloys.** Some metals, when melted together, thoroughly intermix, and on cooling form a metallic-looking substance called an *alloy*. Brass, composed of zinc and copper, is a familiar example of an alloy. Not all metals will mix in this way, and in many cases there is a limit to the solubility

of one metal in the other. Upon solidifying, the solution sometimes remains entirely homogeneous in character, just as it was in the liquid condition. It is then called a *solid solution*; brass is an example. Sometimes definite crystals of a compound of the two metals separate as the solution cools, thus destroying the uniform character of the alloy.

**The eutectic.** In general the melting point of any metal is lowered by having another metal dissolved in it. Consequently the melting point of an alloy is below the average of the melting points of its constituents, and it is usually lower than that of any one of them. It is evident that if we melt two or more metals together in all possible proportions, we shall obtain one particular mixture that will melt at a lower temperature than any other mixture. This mixture is called the *eutectic*, and its melting point is called the eutectic temperature. Many commercial alloys are eutectics of two or more metals.

**Eutectic diagram.** In the diagram (Fig. 130) let us indicate the composition of the alloy along the line  $AB$  divided into 100 divisions. Let  $A = 100$  per cent antimony and  $B = 100$  per cent lead.  $C$ , which is halfway between  $A$  and  $B$ , will then represent 50 per cent each of antimony and of lead, and  $E''$  80 per cent lead and 20 per cent antimony.

The vertical lines  $AT$  and  $BT$  represent temperature,  $A'$  being the melting point of antimony and  $B'$  that of lead.

If to pure lead we add a small percentage of antimony, the freezing point is lowered, the fall with increasing quantities of antimony being shown by the sloping line  $B'E$ . Similarly, if to pure antimony we add increasing quantities of lead, the fall in freezing point is shown on the sloping line  $A'E$ . The point  $E$  ( $228^\circ$ ) is thus the lowest temperature at which any mixture of antimony and lead can remain liquid, and is therefore the *eutectic temperature*. The composition of the liquid at this point ( $E''$ ) is called the *eutectic composition*.

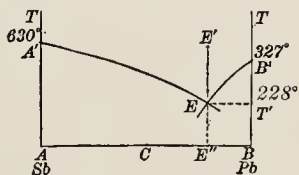


FIG. 130. Diagram illustrating the eutectic of antimony and lead

**Alloys of antimony and bismuth.** Both antimony and bismuth readily alloy with many other metals. The alloys so formed are heavy, are easily melted, do not oxidize easily or act upon water, and, in general, are well adapted to many technical uses. The manufacture of alloys constitutes the chief use of these two metals.

Antimony imparts to its alloys the property of expanding slightly in solidification, which renders them especially useful in type founding, where fine lines are to be reproduced on a

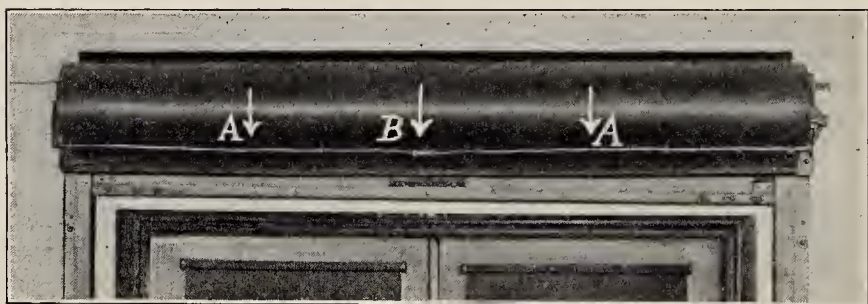


FIG. 131. Picture of an automatic fire curtain

cast. *Type metal* consists of antimony, lead, and tin. *Babbitt metal*, used for journal bearings in machinery, contains the same metals in a different proportion, together with a small percentage of copper.

Bismuth is particularly valuable in the production of very low-melting alloys. For example, *Wood's metal*, consisting of bismuth, lead, tin, and cadmium, melts at  $60.5^{\circ}$ . The low melting point of such alloys is turned to practical account in making automatic fire curtains and automatic water sprinklers in buildings, safety plugs in boilers, and many similar devices.

Fig. 131 shows a fire curtain, which is held in place by two wires (A, A) joined at B by a bismuth alloy. In case of fire the alloy melts, and the wires holding the curtain up are thereby released and the curtain drops, covering the door.



## ALLOYS OF ANTIMONY AND BISMUTH

NAME	LEAD	TIN	ANTI-MONY	BIS-MUTH	
Type metal (older) . .	50.0	25.0	25.0		Copper 3.0
Type metal (newer) . .	60.0	10.0	30.0		
Pewter . . . . .	20.0		80.0		
Britannia metal . . . .		90.0	7.0		
Antifriction metal (Babbitt metal) . . .	66.0	17.0	17.0		
Fusible metals					Cadmium 12.5
Rose's (m. p. 93.8°) .	25.0	25.0		50.0	
Wood's (m. p. 60.5°)	25.0	12.5		50.0	
Newton's (m. p. 94.5°)	31.25	18.75		50.0	

## EXERCISES

1. What is the derivation of the word *phosphorus*?
2. What compounds should you expect phosphorus to form with bromine and iodine? Write the equations showing the action of water on these compounds.
3. In the preparation of phosphine why is coal gas passed into the flask? What other gases would serve the same purpose?
4. Give the formula for the salt which phosphine forms with hydriodic acid. Give the name of the compound.
5. Could phosphoric acid be substituted for sulfuric acid in the preparation of the common acids?
6. Write the equations for the preparation of the three sodium salts of orthophosphoric acid.
7. Why does a solution of normal sodium phosphate show an alkaline reaction?
8. If arsenopyrite is heated in a current of air, what products are formed?
9. (a) Write equations for the complete combustion of hydrogen sulfide, methane ( $\text{CH}_4$ ), and arsine. (b) In what respects are the reactions similar?
10. Write the equations for all the reactions involved in Marsh's test for arsenic.
11. Write the names and formulas for the acids of antimony.

12. Write the equations showing the hydrolysis of antimony trichloride; of bismuth nitrate.

13. In what respects does nitrogen resemble the members of the phosphorus family?

14. A phosphate rock used as a source of phosphorus in the preparation of the element contained 80 per cent of calcium phosphate. Assuming that 10 per cent of the phosphorus is not liberated, what weight of the rock will be required to meet the needs of a plant preparing 50 tons of phosphorus monthly?

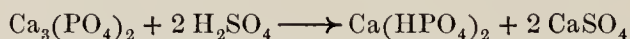
15. What weight of arsenic trioxide can be prepared from 1 kg. of arsenopyrite?

16. Suppose you wish to prepare 1 kg. of bismuth oxychloride; what weight of bismuth would be required?

17. What weight of stibnite is necessary for the preparation of 10 kg. of antimony?

18. What weight of phosphorus is required to make 100 kg. of pure phosphoric acid (hydrogen phosphate)?

19. In the manufacture of fertilizers what weight of 50 per cent sulfuric acid is required for the treatment of 1 ton of phosphate rock containing 80 per cent calcium phosphate, assuming that the reaction is as follows:



20. A compound, upon analysis, was found to have the following composition: Ca, 38.74 per cent; P, 20.01 per cent; O, 41.24 per cent. Calculate its simplest formula.

## CHAPTER XXV

### SILICON ; TITANIUM ; BORON

NAME OF ELEMENT	SYMBOL	ATOMIC WEIGHT	DENSITY	CHLORIDES	OXIDES
Silicon . . . . .	Si	28.06	2.4	SiCl <sub>4</sub>	SiO <sub>2</sub>
Titanium . . . . .	Ti	47.90	4.5	TiCl <sub>4</sub>	TiO <sub>2</sub>
Boron . . . . .	B	10.82	2(?)	BCl <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>

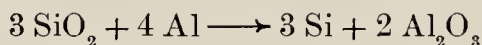
**Introduction.** We have just seen that the elements in the phosphorus family become more and more metallic with increasing atomic weight until we reach bismuth, which is wholly metallic. In Groups III and IV in the periodic table the elements of small atomic weight are acid-forming, while those of larger atomic weight are metals. It will be convenient to consider the acid-forming elements of both groups together at this point, and defer the metals to later chapters.

### SILICON

**Occurrence.** Just as carbon seems to play the most important part in living matter (plants and animals), so silicon plays the same rôle in the compounds that constitute the soils and the rocks that make up the earth's crust. Next to oxygen it is the most abundant element, for the solid crust of the earth is estimated to contain 28 per cent of this element. All varieties of granite, gneiss, sandstone, shale, clay, and marl contain large percentages of silicon ; limestone and dolomite are the only important geological formations measurably free from it. To some extent its compounds are assimilated by plants and animals, and silicon compounds constitute the outer shell of many aquatic organisms.

**Properties of silicon.** The element presents a close analogy with carbon in that it can be obtained in amorphous form as well as in crystals resembling the diamond. These crystals are very hard, easily scratching glass, and have a density of 2.40. They melt at about  $1420^{\circ}$ . A lump of the element is very brittle and breaks with a crystalline fracture which has a metallic, silvery appearance.

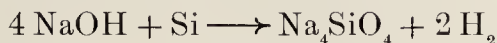
**Preparation.** In the laboratory crystallized silicon is best prepared by the reduction of the dioxide with aluminum:



The silicon dissolves in the excess of melted aluminum, and when the solution has cooled and become solid, the aluminum is dissolved in hydrochloric acid, the silicon being left in the form of shining metallic needles. The reduction of the dioxide with carbon has always presented the difficulty that the reduced element tends to combine with excess of carbon to form a carbide. This difficulty has been overcome to a great extent, and nearly pure silicon is now manufactured in large quantities. By reducing a mixture of the oxides of silicon and iron with carbon an alloy of the two elements, called *ferrosilicon*, is obtained. This alloy, as well as the purer silicon, finds an important application in the metallurgy of iron.

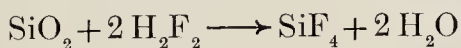
**Chemical conduct.** At ordinary temperatures silicon is inactive. It is most easily attacked by the halogens, forming gaseous compounds such as  $\text{SiCl}_4$ . At high temperatures it combines with most elements, forming *silicides*, such as those of magnesium ( $\text{Mg}_2\text{Si}$ ) and carbon ( $\text{CSi}$ ). It is not attacked by oxygen as easily as we should expect, considering the difficulty with which the oxide is reduced. This is due to the high melting point of both the metal and its oxide, and to the fact that a film of nonvolatile oxide, forming on the surface of the metal, protects it from further action. It acts upon the alkalis, evolving hydrogen and forming soluble

silicates,—a reaction sometimes used in the commercial preparation of hydrogen (p. 46):

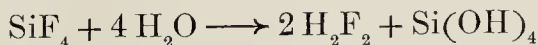


**Compounds of silicon with hydrogen and the halogens.** Silicon hydride ( $\text{SiH}_4$ ) corresponds in formula to methane ( $\text{CH}_4$ ), but its properties are more like those of phosphine ( $\text{PH}_3$ ). It is a very inflammable gas of disagreeable odor and, as ordinarily prepared, takes fire spontaneously on account of the presence of impurities.

Silicon combines with the elements of the chlorine family to form such compounds as  $\text{SiCl}_4$  and  $\text{SiF}_4$ . Of these silicon fluoride ( $\text{SiF}_4$ ) is the most familiar and interesting. As stated in the discussion of fluorine (p. 304), it is formed when hydrofluoric acid acts on silicon dioxide or on a silicate. With silica the reaction is as follows:



Silicon fluoride is a very volatile, invisible, poisonous gas. In contact with water it is partially decomposed, as shown in the equation



The hydrofluoric acid so formed combines with an additional amount of silicon fluoride, forming the complex *fluosilicic acid* ( $\text{H}_2\text{SiF}_6$ ), thus:

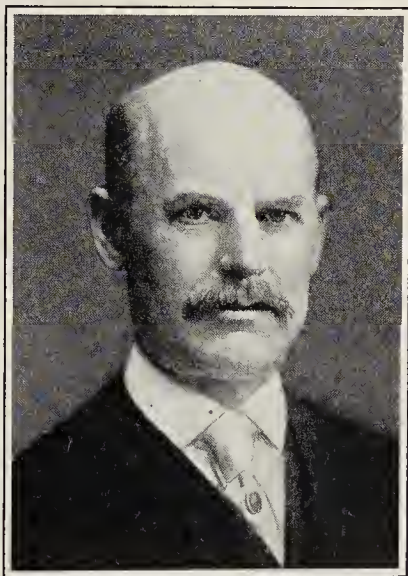
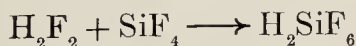


FIG. 132. Edward Goodrich Acheson (1856- )

An American scientist who discovered commercial methods for the manufacture of carborundum, graphite, and a number of similar products of great use in the industrial world



**Silicides.** As the name indicates, silicides are compounds consisting of silicon and some one other element. They are very stable at high temperatures and are usually made by heating the appropriate substances in an electric furnace.

The most important silicide is carbon silicide (CSi), known in commerce variously as *carborundum*, *crystolon*, or *carbolon*.

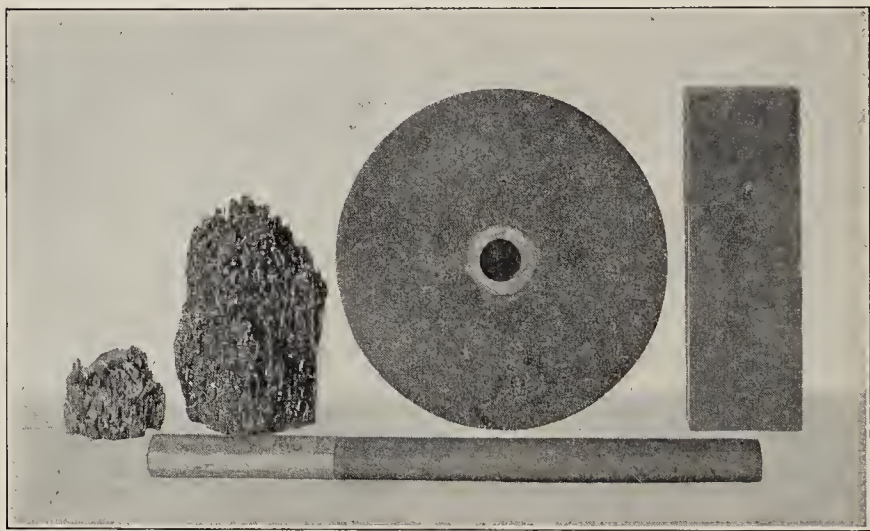


FIG. 133. Crystals of silicon carbide (carborundum) and some abrasives made from the carbide

It is made by heating coke and sand in an electric furnace, — a process devised by Acheson (Fig. 132) in 1891 and extensively carried on at Niagara Falls. The following equation represents the reaction :



The substance so prepared consists of beautiful purplish-black crystals, which are surpassed in hardness only by a few substances, such as the diamond and boron carbide. Silicon carbide is used as an *abrasive* for grinding and polishing very hard substances. Fig. 133 shows two samples of the crystalline material, as well as a whetstone and a grinding wheel prepared from silicon carbide, illustrating some of its many uses.

**Manufacture of silicon carbide.** The materials used in making silicon carbide are carbon, sand, common salt, and sawdust. The salt assists in the reaction, while the sawdust burns away, leaving

the mass porous and thus allowing the escape of gases. The mixture of materials is heated in a large resistance furnace, similar to the one employed in the manufacture of graphite (p. 134). Fig. 134 represents a cross section of

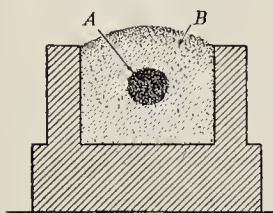


FIG. 134. Diagram showing the cross section of a charged carborundum furnace before heating

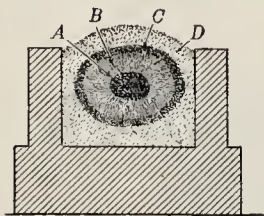


FIG. 135. Diagram showing the cross section of a charged carborundum furnace after heating

the furnace after charging, *A* being the carbon core and *B* the coke and sand. Fig. 135 shows the appearance after heating. *A* is the core of the carbon, surrounded by silicon carbide *B*. Around this is a shell of amorphous carbide *C*, while *D* is unchanged charge.

### Silicon dioxide (silica)

( $\text{SiO}_2$ ). This substance

is found in nature, both in the amorphous and in the crystalline condition.

In the form of *quartz* (Fig. 136) it is found in six-sided prisms, sometimes of great size. When pure it is perfectly transparent and colorless.

Some colored varieties are given special names, as *amethyst* (violet), *rose quartz* (pale pink), *smoky* or *milky quartz* (colored and opaque). Other varieties of silicon dioxide, some of which also contain water, are *chalcedony*, *onyx*, *jasper*, *opal*, *agate*, and *flint*. *Sand* and *sandstone* are largely silicon dioxide.



FIG. 136. A cluster of quartz crystals

The skeletons of certain microörganisms (infusoria) are composed of nearly pure silica. In some localities these have accumulated in immense deposits, forming a very fine and sharp sand called *infusorial earth*. This material is often used as a scouring-powder, especially in scouring-soaps.

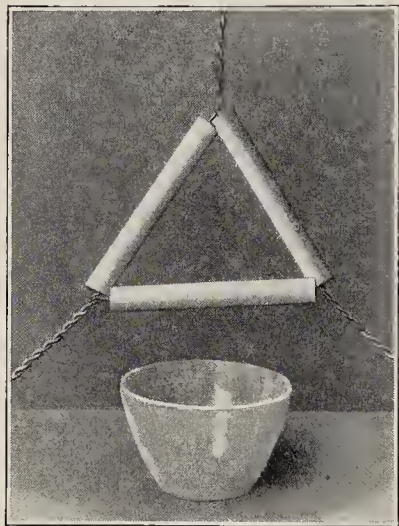
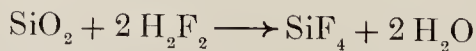


FIG. 137. Picture of a crucible and a triangle made from silica

**Properties.** As obtained by chemical processes silicon dioxide is an amorphous white powder. In the crystallized state it is very hard and has a density of 2.6. Pure silica begins to soften at about 1600°, and somewhat above this temperature it can be drawn out into threads, blown like glass into tubes and small vessels, and molded into large bowls and pipes for use in chemical industries. These articles (Fig. 137) are attacked by comparatively

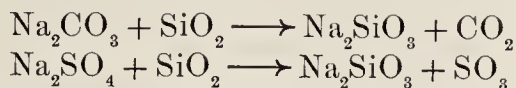
few ordinary reagents, and they do not expand or contract to any appreciable extent with even very great changes in temperature. On this account a quartz vessel can be heated red-hot and plunged into cold water without cracking.

**Chemical conduct.** Silica is insoluble in water and in most acids. It is very stable, so that the oxygen which it contains can be removed only by the most powerful reducing agents and at very high temperatures. Hydrofluoric acid attacks it readily (p. 304), according to the equation



Since it is the anhydride of an acid (p. 236), it dissolves in fused alkalis to form *silicates*. Being nonvolatile, it will drive out most other anhydrides when it is heated with their salts

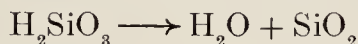
to a high temperature, especially when the silicates so formed are fusible (p. 245). The following equations illustrate this property :



**Simple silicic acids.** Silicon forms two simple acids, *orthosilicic acid* ( $\text{H}_4\text{SiO}_4$ ) and *metasilicic acid* ( $\text{H}_2\text{SiO}_3$ ). Orthosilicic acid is set free as a jellylike mass when orthosilicates are treated with strong acids. If one attempts to dry this acid, it loses water, passing into metasilicic acid :



Metasilicic acid, when heated, breaks up into silica and water, thus :



Both of these silicic acids are very weak, and their soluble salts are much hydrolyzed in solution.

**Salts of silicic acids; silicates.** A number of salts of the orthosilicic and metasilicic acids occur in nature. Thus, *mica* ( $\text{KAlSiO}_4$ ) is a mixed salt of orthosilicic acid, and *wollastonite* ( $\text{CaSiO}_3$ ) is a metasilicate.

**Condensed silicic acids.** Silicon has the power to form a great many complex acids which may be regarded as derived from the union of several molecules of orthosilicic acid, with the loss of water. These are called *condensed silicic acids*. For example, we have



Salts of these condensed acids make up the great bulk of the earth's crust. The feldspar known as *orthoclase*, for example, has the formula  $\text{KAlSi}_3\text{O}_8$  and is a mixed salt of the acid  $\text{H}_4\text{Si}_3\text{O}_8$ , whose formation is represented in the equation above. *Kaolin*, or pure clay, has the formula  $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$  or, as it is commonly written,  $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2 \text{H}_2\text{O}$ . *Granite* is composed of crystals of feldspar and mica cemented together with amorphous silica.



**Water glass.** A concentrated solution of a mixture of sodium silicates or of potassium silicates or of both is called *water glass*. It is a thick, sticky liquid made by fusing sand with the carbonate of sodium or of potassium. It is strongly alkaline in reaction, owing to the ready hydrolysis of these salts. It is used for the purpose of giving a glazed waterproof surface to porous materials, such as wood, stone, and plaster; to render curtains noninflammable; as a glue for glass and pottery and paste-board boxes; and as an ingredient in cheap soaps.

Its property of closing pores is turned to account in the preserving of eggs for winter use. The eggs are packed in crocks and then covered with a liquid made by adding 1 volume of commercial water glass to 10 volumes of water. Over the liquid is then poured a little melted paraffin, which soon hardens and excludes the air. Fresh eggs can be preserved for from six to eight months in this way.

## TITANIUM

**Occurrence.** Titanium is an abundant element, ranking ninth among the elements in this respect, and surpassing both carbon and sulfur in abundance. In general it is very widely scattered, constituting about 0.5 per cent of all soils.

In more concentrated form it is usually found as the dioxide  $\text{TiO}_2$ , called *rutile*, or as an iron titanite ( $\text{FeTiO}_3$ ) known as *ilmenite*, or as a variable constituent of certain magnetic iron ores. Most of the rutile used is mined in Virginia.

**The element.** The element can be obtained by the reduction of the dioxide with carbon in an electric furnace, but prepared in this way it always contains carbon and usually nitrogen. Very pure specimens have been prepared by the action of titanium chloride on sodium in a closed steel bomb:



When the element contains carbon it is hard and very brittle. Its melting point is above that of platinum, being about  $1800^\circ$ . Its specific gravity is 4.5.



An alloy known as *ferrotitanium* is made by reducing iron ores rich in titanium with carbon. This alloy is manufactured on a large scale at Niagara Falls and is used in preparing titanium steel. An average sample contains 15.5 per cent of titanium, 1.4 per cent of silicon, 7.5 per cent of carbon, and 74.3 per cent of iron.

At high temperatures titanium shows a very marked tendency to unite with nitrogen, the nitride  $\text{TiN}$  being the product of this direct union. The nitride is therefore always produced in any attempt to prepare titanium in an apparatus to which air has access, and this compound was formerly considered to be the element itself. When iron ores containing titanium are smelted, a substance in appearance resembling crystallized copper is often found in the slag or adhering to the lining of the furnace. This was also at one time supposed to be the metal, but is now known to be a compound or perhaps a mixture of compounds containing variable quantities of titanium, carbon, and nitrogen. It is called *titanium carbonitride*.

**The compounds.** The compounds of titanium very closely resemble those of silicon. The dioxide of titanium, like that of silicon, is an acid anhydride and forms a large number of acids closely resembling the various types of silicic acids. These are even weaker than those of silicon, and their salts hydrolyze more readily. Fluotitanic acid ( $\text{H}_2\text{TiF}_6$ ) and its salts are well known. The dioxide  $\text{TiO}_2$ , mixed with barium sulfate, is known as *titanox* and is a valuable pigment for white paints. Titanium tetrachloride ( $\text{TiCl}_4$ ) is easily made by passing chlorine over the carbonitride. It is a fuming liquid and was used somewhat in the World War for the production of smoke screens.

Unlike silicon, titanium also forms salts in which the element acts as a tervalent metal. The titanic salts are formed by the action of nascent hydrogen upon derivatives of the dioxide. The sulfate  $\text{Ti}_2(\text{SO}_4)_3$  and the chloride  $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$  are examples. These salts are either green or violet in color.

## ZIRCONIUM

Zirconium is a rare element found in nature chiefly as the silicate  $\text{ZrSiO}_4$ , called *zircon*, and as the dioxide  $\text{ZrO}_2$ , or *zirconia*. A large deposit of this compound occurs in Brazil. The dioxide is very difficultly fusible, melting at about  $3000^\circ$ . To some extent it is used in making refractory bricks for lining small furnaces.

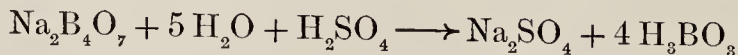
## BORON

**Occurrence.** Boron occurs in nature as *boric acid* ( $\text{H}_3\text{BO}_3$ ) and in salts of *condensed boric acids*, which usually have very complicated formulas.

**Preparation and properties.** The element boron is extremely difficult to prepare in pure condition, and it is known only in an amorphous state. It is a gray powder which melts at about  $2300^\circ$ . In hardness it closely approaches the diamond. It can be prepared by methods similar to those used in preparing silicon.

**Boric acid ( $\text{H}_3\text{BO}_3$ ).** This compound is found dissolved in the water of hot springs in some localities, particularly in Italy. Being volatile with steam, boric acid is present in the vapor from these springs. The acid is easily obtained from these sources by condensation and evaporation, the necessary heat being supplied by other hot springs.

It is often prepared by treating a strong hot solution of borax ( $\text{Na}_2\text{B}_4\text{O}_7$ ) with sulfuric acid. Boric acid, being but sparingly soluble in water, crystallizes out on cooling:

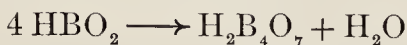


Boric acid crystallizes in pearly flakes which are slippery to the touch. It is a mild antiseptic and is often used in medicine, particularly for eyewashes. Its acid properties are extremely weak. When heated to fusion it is converted into *boric oxide* ( $\text{B}_2\text{O}_3$ ).

**Metaboric acid and tetraboric acid.** When boric acid is gently heated, it is converted into metaboric acid ( $\text{HBO}_2$ ):



On heating metaboric acid to a somewhat higher temperature *tetraboric acid* ( $\text{H}_2\text{B}_4\text{O}_7$ ) is formed:



**Sodium tetraborate ( $\text{Na}_2\text{B}_4\text{O}_7$ ).** If we add sodium hydroxide to boric acid we do not get a salt of the simple acid, but one that has the formula  $\text{Na}_2\text{B}_4\text{O}_7$  and is called *sodium tetraborate*. When this is crystallized from water at ordinary temperatures the crystals are composed of this salt, together with water, and have the formula  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ . This compound is called *borax*.

**Borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ ).** Borax is the most important compound of boron. It usually has the formula just indicated, but if it is crystallized from hot solutions the pentahydrate  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5 \text{H}_2\text{O}$  is obtained. It is found in some arid countries, as southern California and Tibet, but is now made commercially from the mineral *rasorite*, which has the composition expressed by the formula  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4 \text{H}_2\text{O}$ . It will be noted that borax differs from rasorite only in the percentage of water of hydration present, so that its preparation from the mineral is easily carried out.

When borax is heated, it swells up in a sort of froth, owing to the escape of steam, and this soon melts to a clear glass. The glass has the property of easily dissolving many metallic oxides, and this fact is turned to account in working with metals. When two pieces of metal are to be joined by melting them together or by the use of some kind of solder, the surfaces must be clean and free from oxide. Brass is joined by melting borax over the joint to clean the metal, and then using a low-melting brass as a solder (brazing). Metallic oxides dissolved in melted borax often color the

borax glass with characteristic tints. On this account little beads of borax are used in testing for the presence of such metals.

Borax is extensively used as a constituent of glass of certain kinds, and of enamels and glazes for both metal ware and pottery. It is often used in our homes to soften hard water, as a mild alkali (like soap), and as an antiseptic. The United States uses annually about 40,000 tons of borax and boric acid.

The reason why metallic oxides dissolve in borax is that borax contains an excess of acid anhydride, as can be more easily seen if its formula is written  $2\text{NaBO}_2 + \text{B}_2\text{O}_3$ . The metallic oxide combines with this excess of acid anhydride, forming a mixed salt of metaboric acid.

#### EXERCISES

1. What is the action of a solution of borax on litmus? Explain fully.
2. Carbon and silicon are in the same group in the periodic arrangement of the elements. Point out any resemblance between the two elements.
3. What compound would result by the complete hydrolysis of silicon tetrachloride ( $\text{SiCl}_4$ )?
4. Give the composition of the following minerals: (a) quartz; (b) opal; (c) mica; (d) kaolin; (e) orthoclase; (f) rutile; (g) rasorite.
5. (a) Orthoclase is a salt of what acid? (b) Show how this acid may be regarded as derived from orthosilicic acid.
6. Which has the greater percentage of silicon, kaolin or feldspar?
7. 100 kg. of ordinary borax contains what weight of water of crystallization?
8. What weight of rasorite is necessary for the preparation of 1000 kg. of ordinary borax, on the supposition that all the boron in the colemanite is converted into borax?

## CHAPTER XXVI

### THE COLLOIDAL STATE OF MATTER

**Introduction.** We all know that coarse sand shaken up with water quickly settles when we stop shaking the mixture. The finer the sand the more slowly it settles. If we powder it fine enough and then stir it into water, it will not settle at all, for the particles will be so small that they will be kept in constant motion by collision with the fast-moving molecules of the water. If we could powder the sand into individual molecules and stir them into water, we should have a true solution.

In this chapter we shall be interested in these very fine particles which are too small to settle or to be filtered from the solvent, which cannot be seen directly by even the best of microscopes, and which yet consist of many thousands of molecules. Such particles suspended in a liquid constitute a *colloidal system*. The particles are said to be in a *colloidal state* and *dispersed* through the liquid. Moreover, we speak of the small particles as the *dispersed phase*, and the liquid as the *dispersing phase*. The term *colloidal solution* is sometimes used, but it is evident that this is a misnomer.

**Colloids.** It was formerly thought that a certain definite group of substances, nearly all of an amorphous character, were the only ones that could assume the colloidal state, and such substances were called *colloids*. The opposite of the colloid was the *crystalloid*, which formed a true solution and could not be obtained in the colloidal state. We now know that *any* substance can be obtained in the colloidal state in any liquid in which it is very little soluble; and that there is no definite class of substances that can properly be called colloids. Some substances, however, such as starch and gelatin, have a very great tendency to assume the colloidal state, and we often call such substances colloids.



**Tyndall effect.** The air in a quiet room contains many particles of colloidal size that are too small to be seen as objects even through a microscope. But if the room is dark and a beam of sunshine enters through a small hole, these minute

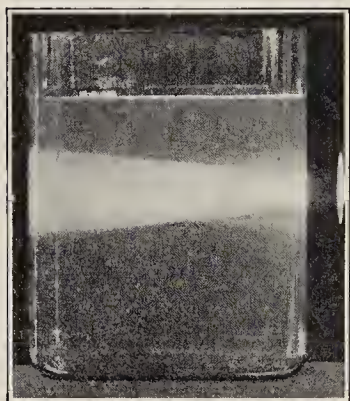


FIG. 138. Picture of a beam of light shining through a colloidal dispersion, showing the Tyndall effect

particles can be seen as bright, flashing points, or motes, dancing in the sunbeam. In like manner a liquid containing a dispersed colloid that appears perfectly clear to the eye is seen to be full of moving particles when a strong beam of light shines through the liquid (Fig. 138). Such a beam of light, illumined by colloidal particles, is called the *Tyndall effect* or the *Tyndall cone*.

**Ultramicroscope.** If we arrange a microscope perpendicular to a Tyndall cone produced in a colloidal dispersion, we can see innumerable spots of light moving in zigzag paths at all sorts of speeds (Fig. 139). This movement is called the *Brownian movement*, after the English botanist Brown, who first observed it. It is a confirmation of the kinetic conception of gases and liquids, for in it we actually witness the movement of particles.

An instrument consisting of a microscope and appliances for illumining brilliantly a few drops of a colloidal dispersion is called an *ultramicroscope*. With it we do not see any real *objects*, for colloidal particles are submicroscopic in size; we see merely the light refracted by these particles.

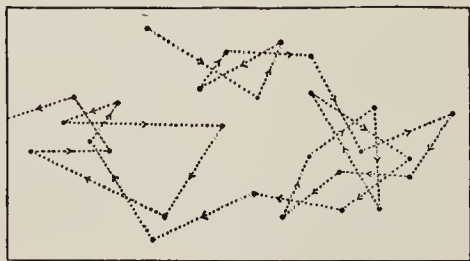


FIG. 139. Diagram illustrating the Brownian movement

**Size of colloidal particles.** There are no definite limits that we can place upon the size of particles that will entitle them to be considered colloidal. In general, however, all particles between 1 and 100 millimicrons in diameter show very pronounced colloidal characteristics. (A millimicron is one millionth of a millimeter.) The smallest particle that we can see with an ultramicroscope is about 1 millimicron in diameter and consists of about 10,000 molecules of ordinary size.

**Varieties of colloidal dispersions.** We have already seen some resemblance between a colloidal dispersion in a liquid and dust particles in the air. When the particles in the air are numerous enough, we call the mass *smoke*. In a similar way a very fine suspension of droplets of water in air is called *fog*. A liquid full of droplets of another liquid is an *emulsion*; a liquid full of minute bubbles of a gas is *foam*. All these are properly called colloidal dispersions, for they all consist of one form of matter in a very finely divided state scattered through another form.

**Methods of preparing colloidal dispersions.** There are many ways of preparing colloidal dispersions, but all these may be classified into two groups:

1. **Dispersion methods.** We may start with an insoluble material (either solid or liquid) and in some way reduce it to the size of particles necessary for colloidal dispersion, and we may then mix these particles in the desired medium. For example, we can prepare a colloidal dispersion of gold, silver, or platinum by producing an electric arc between the ends of two wires of these metals immersed in water (Fig. 140). The current tears off minute particles and disperses them through the water. Almost any sample of ocean water shows traces of colloidal gold reduced to colloidal size by the processes of nature.

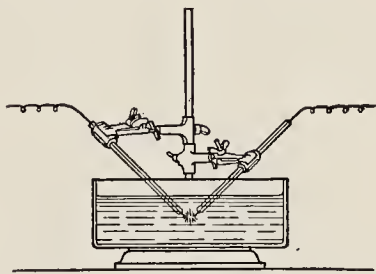


FIG. 140. Diagram illustrating the preparation of metallic colloids by sparking under water

In many cases we may treat finely divided solids (preferably precipitates) by some reagent that does not act upon them in a definite chemical way but does cause them to break up into a colloidal dispersion. Thus, dilute alkali causes the finer particles of clay to form a colloidal dispersion. This action is called *peptization*, and the reagent is said to *peptize* the precipitate.

2. *Condensation methods.* We may start with a solution or a gas and bring about the production of a solid in a finely divided state. For example, we may pass hydrogen sulfide into a neutral solution of a salt of antimony (tartar emetic) and so produce colloidal antimony sulfide ( $\text{Sb}_2\text{S}_3$ ); or we may add an acid to a solution of sodium thiosulfate and produce colloidal sulfur; or we may treat a very dilute solution of gold chloride with ferrous sulfate and obtain colloidal gold.

All these processes result in producing an insoluble solid that gathers into clumps of colloidal size and *then stops growing*. Further growth would result in precipitation. Indeed,

some chemists think that the formation of colloid clumps is always the first step in precipitation.

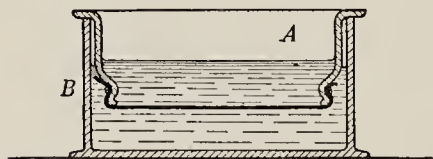


FIG. 141. Diagram of apparatus used in the process of dialysis

**Purification of colloids: dialysis.** If we filter a colloidal dispersion through even the

best of filter paper, no solid is retained on the paper. If we use a fine parchment paper or an animal membrane, we find that the colloidal particles are now prevented from passing through the filter. By taking advantage of this fact we may purify a colloidal dispersion by a process called *dialysis*. The membrane is stretched on a frame like a tambourine, constituting a *dialyzer* (Fig. 141). The colloidal dispersion *A* is placed within it and is partially immersed in pure water *B*. The impurities that are in true solution diffuse through the membrane, while the colloid particles remain, and the dispersion is thus purified.

**Color of colloidal dispersion.** Many colloidal dispersions are highly colored, but the color gives us little clue as to what is present. Particles of a certain size absorb certain wave lengths of light and reflect others, so the color depends primarily upon the size of the particle rather than its character. Thus, colloidal gold may be red, blue, green, or violet, according to the size and uniformity of the particles. A little ferric chloride added to boiling water gives a deep-red colloidal iron oxide.

It takes very little of the colloidal substance to make an intense color. A few milligrams of gold will color a liter of water. A very little of the element selenium added to glass makes the intensely red glass of the automobile tail-light. Many colored glasses and glazes owe their color to colloidal material of various sorts, and many gems are colored in the same way. The blue of the sky and of deep mountain lakes is probably due to colloidal dust in the air and the water.

**Electrical charge of colloidal particles.** Colloidal dispersions are moderately good conductors and therefore contain charged ions. The colloidal particles do not seem to break up into two kinds of ions, but the whole particle appears to move toward one or the other electrode. Some colloids, including most of the metallic oxides, are positively charged; others, including many metallic sulfides, gold, platinum, silver, and silicic acid, are negatively charged. It appears most probable that colloidal particles get their charges by the adsorption into their mass of some simple ions already existing in the solution (most frequently the hydrogen ion  $H^+$  or the hydroxyl ion  $OH^-$ ), much as a cork might "adsorb" a tack when pressed upon it. In an electrical field the imprisoned ion is attracted to the electrode, dragging the whole colloidal clump with it, just as the tack would be attracted by a magnet and carry the cork along with it.

**Adsorption.** By *adsorption* the chemist means the adherence of molecules or ions of any kind to the *surface* of a solid, while by *absorption* he means the penetration of the molecules or ions



into the *interior* of the solid. In reality it is very hard to preserve the distinction, since so many solids are very porous.

The adsorption of an ion by a colloid particle represents in miniature a process which goes on constantly with masses larger than colloids, and which is of great importance in the arts and industries. Certain materials, such as charcoal, adsorb almost incredible quantities of gases or of liquids. For this reason charcoal was used in masks in the World War to adsorb poisonous gases of certain kinds from the air before it was breathed. Palladium and other metals adsorb hydrogen gas. Dried silica adsorbs water vapor and other gases. In fact, nearly all amorphous solids adsorb most gases to some extent.

Adsorption depends largely upon the *extent of surface* presented by the solid. Consequently the adsorptive power of any solid will depend very largely upon the method of its preparation, the extent of its porosity, and the fineness of its division. It has been estimated that 1 g. of high-grade adsorbing charcoal has a surface of from 100 to 1000 *square meters*.

**Adsorption from solutions.** Some solids suspended in solutions will adsorb dissolved materials from the liquid. The metallic oxides adsorb dyes to form *lakes* or to act as *mordants*. Fuller's earth adsorbs the coloring matter from cottonseed oil in the refining of this for use as a salad oil. Doubtless many catalyzers depend for their efficiency on their adsorbing ability, bringing the reacting substances together at high concentration within their pores, or adsorbing one component in a reversible reaction.

Adsorption is therefore *selective* in character. A given solid will adsorb some gases or liquids but not others. A very good practical example of selective adsorption is the cleansing action of soap. A soap "solution" is a colloidal dispersion of colloidal soap acids and acid salts. These have a greater selective adsorption for grease and dirt than do the usual textile fibers. Consequently fabrics of various kinds are cleansed by the use of soap.



**Coagulation of colloids.** All colloidal particles of a given kind selectively adsorb ions of the same electrical sign, and so the particles tend to repel each other. This is one reason why they do not settle. This repulsion prevents the little particles from uniting to form larger ones which would ultimately produce a precipitate.

If we add an electrolyte to a colloidal dispersion, the large number of charged ions now present tends to diminish this repulsion. An adsorbed ion attracts an ion of opposite sign and binds it to the particle. The particle becomes electrically neutral in this way, and many neutral particles now unite to form a precipitate. This process is called *coagulation*. The amorphous precipitate so formed, made up as it is of a conglomerate of colloidal particles, has many peculiar properties and is called a *gel*. The original dispersed colloid is called a *sol*.

In producing coagulation, bivalent ions are more effective than univalent ones, and trivalent ions are still more effective. For this reason aluminum sulfate is much used in the clarification of river water. If we mix two colloids of opposite sign, such as colloidal iron oxide ( $\text{Fe}_2\text{O}_3(+)$ ) and antimony sulfide ( $\text{Sb}_2\text{S}_3(-)$ ), they mutually precipitate each other in electrically equivalent quantities. Two colloids of the same sign have no such effect upon each other.

**Protecting colloids.** Sometimes a colloidal substance that is naturally unstable is made much more stable by the addition of some other colloidal substance of the same sign. The latter colloid is then called a *protecting colloid*. For example, the coloring matter of black ink is often a rather unstable colloidal substance (iron gallotannate). Gum arabic, starch, or dextrin is added as a protecting colloid to keep the coloring matter from precipitating. In making photographic plates gelatin is added to the colloidal silver salts to keep these dispersed.

**Emulsions.** If we pour together two liquids that do not mix, like kerosene and water, and shake the two violently, we get a milky-looking fluid called an *emulsion*. This consists

of very minute drops of the one liquid dispersed through the other. If we let the emulsion of oil in water stand, it will very soon separate into the original liquids from which it

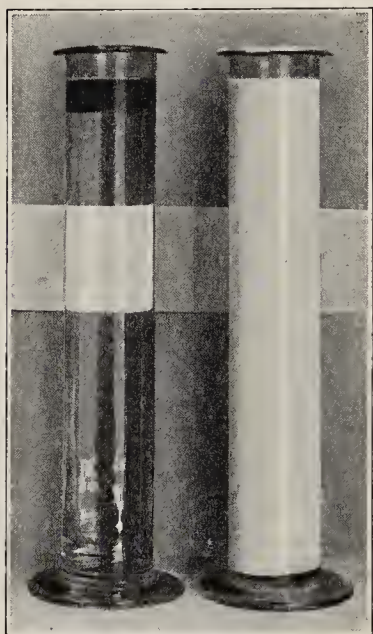


FIG. 142. Emulsions

When oil and water are shaken together, the oil soon separates on standing (A); if a little soap is added to the oil and water, and the mixture shaken, the emulsion becomes more permanent (B)

was made. To make an emulsion of any kind permanent we must add a third colloidal substance, insoluble in both of the liquids. This is called the *emulsifying agent* (Fig. 142). It seems to form a little skin over the surface of the drops and prevents them from running together into big ones. Milk is an emulsion of butter fat in water, with casein as the emulsifying agent. When the milk turns sour (forming an electrolyte acid) and the casein is coagulated, the butter fat is easily collected into large lumps of butter. Most of our common disinfectants and sheep dips owe their properties to cresol (p. 408) emulsified in water, with a small percentage of soap as the emulsifying agent. In mayonnaise, olive oil is emulsified in water (usually with a little vinegar added) by

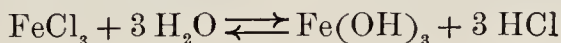
the colloidal yolk of egg, forming a stiff, almost jellylike, product. Cod-liver-oil emulsions contain casein as the emulsifying agent. The fluids that form the webs of spiders and silkworms are secreted as emulsions that almost at once dry to form very fine filaments. Artificial silk closely imitates this process in its mode of manufacture.

Butter is an emulsion of water drops in butter fat, and many lubricating greases are of this same character. The question

as to which liquid forms the dispersed droplets and which one the medium for the dispersion is determined by the nature of the emulsifying agent employed. It seems to act by changing the surface tension of the two liquids to different extents, and surface tension is an important factor in emulsions.

**Emulsion colloids.** Some colloidal particles, as they grow into masses large enough to precipitate, carry with them a large amount of water, so that the gel has the properties of a viscous liquid rather than those of a solid. Such gels are sometimes called *emulsion colloids*. Insoluble metallic hydroxides are usually emulsion colloids of this type. These gels may assume very singular forms, such as flocculent precipitates, thin films, long threads, spongelike structures, and honeycomb cells. A drop of a solution of potassium ferrocyanide added to a solution of copper sulfate or placed in a solution of sodium silicate with a pipette will give an idea of some of these structures.

**Colloids formed by the hydrolysis of salts.** We write the equation for hydrolysis (p. 246) as the reverse of neutralization, thus:



Under favorable conditions no precipitate forms, but the insoluble product of the reaction remains dispersed as a colloid. When it is coagulated, the gelatinous precipitate contains much more water than is represented in the formula  $\text{Fe}(\text{OH})_3$ . In fact, we can get no compound of this formula in this way. What we seem to obtain is really  $\text{Fe}_2\text{O}_3$  holding a variable quantity of water as an emulsion colloid.

**Jellies.** Sometimes a colloidal substance tends to form very thin films rather than particles or threads, and these films may develop in such a way as to inclose the liquid much as the walls of the honeycomb inclose the honey, or the pores of a sponge hold water, or the thin skin of a grape contains the seeds and pulp. When this happens, the whole dispersion is likely to set to a more or less solid form called a *jelly*. Thus,

if we add acid to a solution of sodium silicate, the dilute dispersion of silicic acid which is first formed soon sets to a firm jelly. In fruit jellies it is a constituent of the unripe fruit called *pectin* that serves to form the supporting structure. In gelatin or glue the jelly may be dried out to a very compact form; but when it is dissolved in hot water and cooled, a jelly is once more obtained. When the jelly of silicic acid is dried, it forms solid, infusible lumps resembling a gum. These are extremely porous, owing to the original structure of the jelly, and are very active as catalyzers in many gaseous reactions. Soap is a partially dried jelly, and many minerals such as agate, flint, and opal are dry silica jellies. Photographic films and many high explosives are jellies. Almost any sparingly soluble substance that does not crystallize too readily may be obtained in the form of a jelly. The so-called *solidified alcohol*, used largely at the present time, consists of a porous soap (Chapter XXXIII) and alcohol, the soap acting as a sort of sponge to hold the alcohol.

As yet we do not understand the conditions that lead to the formation of these jellies, and we obtain them largely by accident or by a cut-and-try process.

**Smokes.** Evidently we may have very fine particles suspended in the air rather than in water, and such a suspension is a *smoke*. It is often very hard to condense the particles of a smoke into solid form, and this fact is of enormous industrial importance. Many precious materials literally "go up in smoke" from the stacks of smelters; much zinc is lost as a smoke of zinc oxide in brass foundries; valuable potassium compounds are lost in the smoke of cement burners; and ordinary carbon smoke causes great losses to the individual but profit to the laundries.

**Cottrell process.** All these smoke particles are electrically charged, and the American chemist Cottrell has devised a most effective process for the recovery of smoke particles by causing the smoke to move past metal plates and points charged electrically.



The smoke particles lose their charge and then coagulate, much as a precipitate does, and settle on the sides of the chimney (Fig. 143). The tails of comets are largely made up of particles of colloidal size.

**Fogs and foams.** Fogs consist of very fine droplets of liquid (usually water) suspended in air, so that they correspond to *emulsions*. Foams are gas bubbles dispersed through a liquid. Sometimes these minute gas bubbles are dispersed through what we

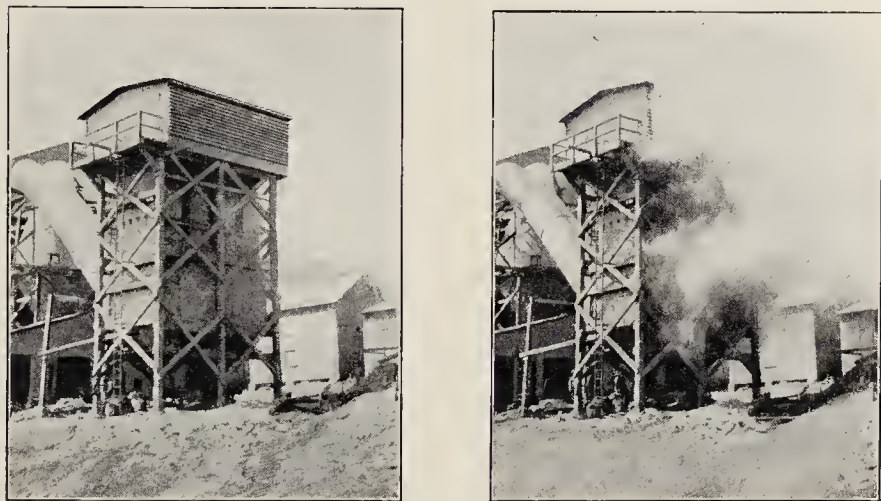


FIG. 143. View of factory showing effect of the Cottrell method for abating dust and smoke

At the left, a factory equipped with Cottrell apparatus; at the right, the same factory not equipped with Cottrell apparatus

should usually consider a solid, and often give to it a pure-white color. Many white flowers, like lilies, owe their whiteness to dispersed gas bubbles, and it appears that white hair is also due to air bubbles in the hair, though no one knows why age or worry should affect the hair in such a way.

**The field of colloids.** It will be seen that an understanding of the fundamental principles of the colloidal state is of the greatest importance. In some cases we wish to break up this condition and bring substances into true solution or to crystallization. In a very much larger number of cases the desirable



properties of substances lie in the fact that they are colloidal, and we wish to produce or maintain this state.

All plastic materials are in part colloidal or closely approach this condition. These include pastes, glues, gums, glasses, cements, rubber, celluloid, clays, etc.

In the organic world the fundamental living cell consists of a colloid wall inclosing a liquid dispersion, very like a jelly. All organs and structures composed of cells have therefore a colloidal character, and nearly all fluids contained in the cells or secreted by them are colloidal dispersions. Consequently physiology and medicine deal constantly with colloidal problems, and all industries that make use of organic materials, such as the manufacture of paper, textiles, and leather, are colloidal industries.

Nearly all the food we eat is colloidal, so that the preparation of food of all sorts is a colloidal art. All preparation of finely divided materials, such as printer's ink and paints, involves colloidal problems. We cannot well overemphasize the importance of extending our knowledge in this field.

### EXERCISES

1. After oil is used in machinery (as in the crank case of an automobile) it becomes very black, and yet very little of the color is removed by ordinary filtration or settling. How do you account for this fact?

2. The term "colloidal solution" is often used. Is it a strictly correct term?

3. Sometimes fruit juices refuse to "jell." Suggest a way of overcoming this difficulty.

4. The white of an egg is a typical colloid. (a) How is it easily coagulated? (b) Is the change a reversible one?

5. Account for the fact that silica occurs in nature in so many different colors.

6. Sodium nitrate ( $\text{NaNO}_3$ ) is a very soluble salt and is largely used as a fertilizer. Why is it not all washed away with the first rain?

7. Point out the difference between electrical conduction in an ordinary electrolyte and in a colloidal dispersion.

## CHAPTER XXVII

### HYDROCARBONS; PETROLEUM

**The hydrocarbons.** In a previous chapter (Chapter XX) attention was called to the fact that carbon is a constituent of a very large number of compounds, over 200,000 having been described. This large number is due in part to the property possessed by carbon of uniting with certain elements in a number of different proportions, thus forming many different compounds with the same element. For example, carbon unites with the element hydrogen to form nearly three hundred different compounds. These compounds of carbon and hydrogen might be called carbon hydrides, but they have long been known as the *hydrocarbons*. *A hydrocarbon, then, may be defined as a compound consisting of carbon and hydrogen only.* Under ordinary conditions some of the hydrocarbons are gases, others are liquids, and still others are solids. Many of them are compounds of the greatest importance, as may be inferred from the fact that certain ones mixed in varying proportions constitute such valuable substances as natural gas, gasoline, kerosene (coal oil), lubricating oils, vaseline, and paraffin, while others serve as the raw material from which are prepared many of our most valuable dyes, medicinal agents, and explosives.

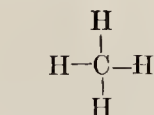
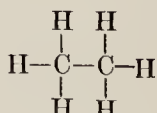
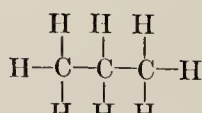
**Classes of hydrocarbons.** Since there are so many hydrocarbons, it is possible, in an introductory course in chemistry, to discuss only a few of the most important ones. In order to simplify their study it is convenient to arrange them in groups or *series*. One of the most important of these series is the *methane series*.

**The methane series of hydrocarbons.** The members of this series are often termed the *paraffin hydrocarbons*, since ordinary paraffin is a mixture of some of the solid members of the series. In the table below are given the names, formulas, and boiling points of some of these compounds. It will be noted that they are arranged in the table in accordance with the number of carbon atoms present. Only the first eight members of the series are given. Others are known, up to those containing as many as 28 carbon atoms.

	BOILING POINT		BOILING POINT
Methane ( $\text{CH}_4$ ) . . .	-161.4°	Pentane ( $\text{C}_5\text{H}_{12}$ ) . . .	+36.2°
Ethane ( $\text{C}_2\text{H}_6$ ) . . .	-88.3°	Hexane ( $\text{C}_6\text{H}_{14}$ ) . . .	+69°
Propane ( $\text{C}_3\text{H}_8$ ) . . .	-44.5°	Heptane ( $\text{C}_7\text{H}_{16}$ ) . . .	+98.4°
Butane ( $\text{C}_4\text{H}_{10}$ ) . . .	+0.6°	Octane ( $\text{C}_8\text{H}_{18}$ ) . . .	+124.6°
General formula, $\text{C}_n\text{H}_{2n+2}$ (in which "n" is the number of carbon atoms)			

A study of the table will show that each member of the series differs from the one preceding it by the group of atoms  $\text{CH}_2$ . Such a series of compounds is called a *homologous series*. In general it may be stated that the members of a homologous series are similar in their chemical conduct and show a regular gradation in some of their physical properties. For example, as revealed in the above table, the boiling points of the compounds gradually increase with each additional  $\text{CH}_2$  group.

**Structural formulas of the hydrocarbons.** The structural formulas of the first three members of the methane series, namely, methane, ethane, and propane, are given below. It will be noticed that in ethane and propane the carbon atoms are joined to each other. It is this property of the carbon atoms of forming connections with each other that helps to make possible the large number of carbon compounds.

Methane ( $\text{CH}_4$ )Ethane ( $\text{C}_2\text{H}_6$ )Propane ( $\text{C}_3\text{H}_8$ )

**Properties and chemical conduct of the hydrocarbons.** The first four members of the methane series, namely, methane, ethane, propane, and butane, are gases under ordinary conditions of temperature and pressure. Those containing from 5 to 16 carbon atoms are liquids, the boiling points of which increase with the number of carbon atoms present; those containing more than 16 carbon atoms are solids. The hydrocarbons are insoluble in water and are not readily acted upon by other compounds; even strong acids and bases have little or no effect upon them. All of them, however, are combustible, the lower members of the series being very readily so. When they burn, both the carbon and the hydrogen unite with oxygen, forming carbon dioxide and water.

**Petroleum.** The great natural source of the methane hydrocarbons is petroleum. This is a dark-colored liquid found stored in the earth in certain localities. It varies somewhat in composition according to the locality in which it is found; in general it is composed of liquid hydrocarbons in which are dissolved both gaseous and solid hydrocarbons, but all of these do not belong to the methane series. At present the chief oil-producing regions in the United States are California, Oklahoma, and Texas. In order to obtain the oil, wells are sunk into the oil-bearing strata, which vary in depth from a few feet to nearly a mile. Sometimes the oil is under such pressure that it will flow to the surface of the earth in large volumes when the opening is made; more often the oil must be pumped to the surface. It is then stored in tanks (Fig. 144) until it is desired to *refine* it. By this process (see page 367) many useful products are obtained; among them are *gasoline*, *kerosene*, *lubricating oils*, *vaseline*, and *paraffin*. These products are not single compounds but are *mixtures of hydrocarbons boiling between certain limits*. Since these oils are derived from petroleum, which is obtained from the earth, they are often termed *mineral oils*, to distinguish them from oils derived from animal and vegetable sources.



The total production of petroleum is very large and is increasing from year to year (Fig. 145) with the demand for the different products obtained from it, especially gasoline. Thus, in 1918 the production in the United States was 355,928,000 barrels of 42 gallons each, while at present it is about 700,000,000 barrels. The United States produces from 70 to 75 per cent of the world's

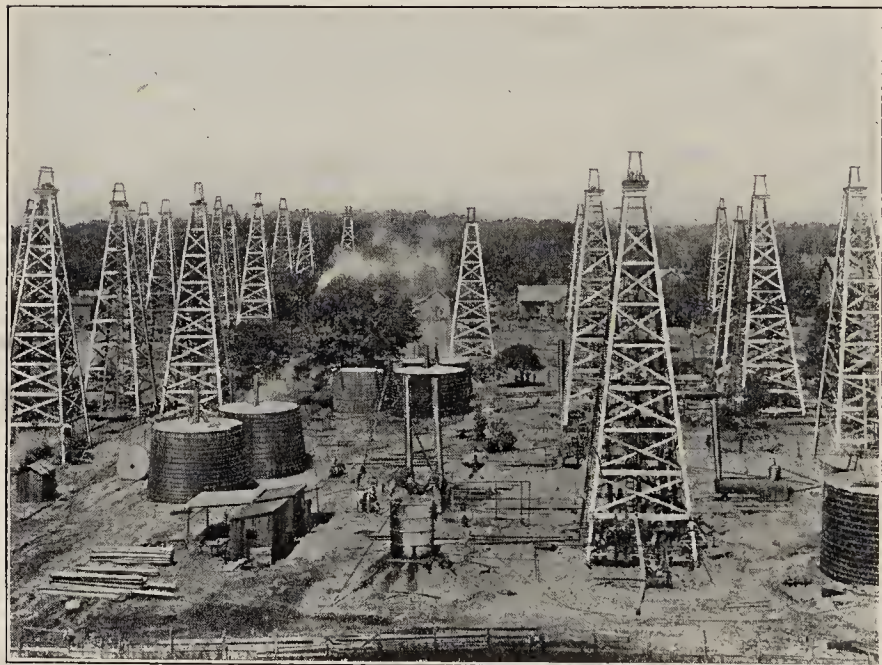


FIG. 144. A typical scene in an oil field

supply, Mexico being the country second in production. Notwithstanding the large consumption of gasoline, the supply at present is equal to the demand. In 1922 the output of gasoline in the United States amounted to over 6,200,000,000 gallons. In 1929 the output had increased to approximately 15,000,000,000 gallons, or a little more than 100 gallons for each inhabitant.

**Fractional distillation.** The process of purifying a mixture such as petroleum is known as *fractional distillation*. In this process the mixture is heated, and in a general way the compounds distill over in the order of their boiling points. By



repeating the process it is ordinarily possible to separate a mixture into the compounds present. In the refining of petroleum it is not necessary to effect such a sharp separation, but only to obtain a mixture of compounds which boil within certain limits.

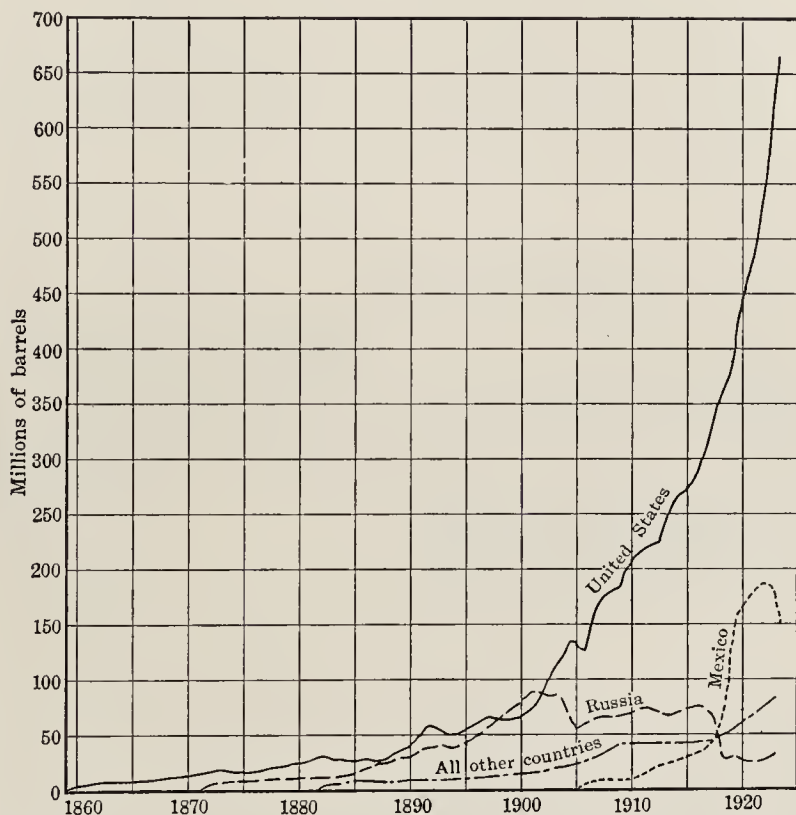


FIG. 145. Curves showing the production of petroleum in the chief oil-producing countries over a number of years

**The refining of petroleum.** The crude oil as it comes from the ground is sometimes used directly as a fuel, but for most purposes it must be *refined*. In this process the oil is run into large iron stills (Fig. 146) and is then distilled. The distillates which pass over between certain limits of temperature are kept separate and, after being purified by treatment with sulfuric acid and then with sodium hydroxide and water, serve for different uses. The liquid passing over between approximately  $70^{\circ}$  and  $150^{\circ}$  is known as

*naphtha*, while that passing over between  $150^{\circ}$  and  $300^{\circ}$  constitutes ordinary *kerosene*. At still higher temperatures the various *lubricating oils* distill over, and finally *vaseline* and the *paraffin oils*. The latter, on being chilled, deposit the solid *paraffin*.

**The naphthas.** A number of different naphthas are recognized commercially, differing in boiling points and density. *Benzine* is a low-boiling naphtha and, being a good solvent for such organic substances as fats and oils, is used in cleaning

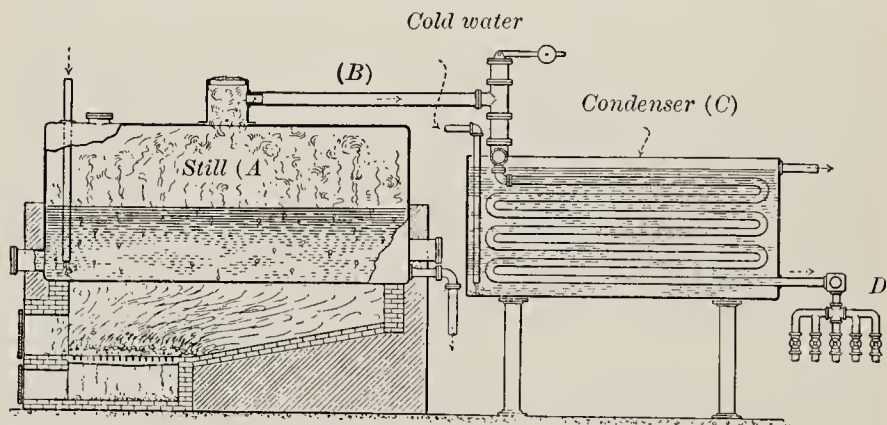


FIG. 146. Diagram of apparatus used for distilling petroleum

The crude oil is run into the large still *A* and heated. The vapors pass off through *B* and are condensed in *C*. The resulting liquids are drawn off through *D*

fabrics (dry-cleaning). Gasoline is a relatively low-boiling naphtha used largely as a source of power in gasoline engines. Some of the higher-boiling naphthas are used in making paints.

**Gasoline as motor fuel.** The use of gasoline as a source of power in engines is based on the facts that the gasoline is readily volatile and that a mixture of gasoline vapor and air, when ignited, burns instantaneously, or, as commonly expressed, explodes. Such a mixture of gasoline vapor and air is conducted into the cylinder of the engine and ignited by an electric spark. The products of the explosion occupy a larger volume than the explosive mixture, and a pressure is thus produced which moves the piston and so runs the engine.

**The cracking of oils.** Formerly kerosene was the most important of the products obtained from petroleum. At present, however, gasoline is by far the most valuable, so that every effort is now made to increase the yield of gasoline. To accomplish this the distillation is carried on under conditions that tend to decompose the larger molecules making up the higher-boiling liquids into the simpler molecules which constitute liquids of lower boiling points. The process is known as the *cracking* of oils. It consists essentially in heating the oils or their vapors under pressure. It is of interest to note that it is possible in this way not only greatly to increase the yield of gasoline obtainable from a given sample of petroleum, but also, by selecting proper conditions of temperature and pressure, to bring about reactions that result in the formation of certain hydrocarbons of the benzene series (p. 407) which are used in making dyes and explosives.

**Use of benzine and gasoline in our homes.** Because of the ease with which benzine and gasoline (these two terms are often used interchangeably) burn, and also because of the explosive character of their vapor when mixed with air, accidents often result from their use, especially when they are employed in our homes for cleaning fabrics. Recent statistics show that in a single year 1040 persons were burned to death and 3120 injured as a result of gasoline fires. It is obvious, therefore, that the greatest care should be exercised in its use.

**Methane (marsh gas) ( $\text{CH}_4$ ).** Methane is the first member of the methane series of hydrocarbons. It is the principal constituent of natural gas. It is formed in marshes by the decay of vegetable matter under water (hence the name *marsh gas*), and bubbles of the gas are often seen to rise when the dead leaves on the bottom of pools are stirred. It sometimes collects in mines, and when mixed with air is called *fire damp* by the miners because of its great inflammability, *damp* being an old name for *gas*. If a flame is brought in contact with such a mixture, very disastrous explosions occur. Methane is formed when organic matter, such as coal or wood, is heated in closed vessels, and is therefore a principal constituent of coal gas. Pure methane is a colorless, odorless gas about one

half as heavy as air. It is but slightly soluble in water. When ignited it burns with a pale-blue flame :

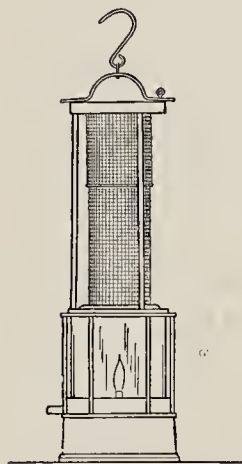
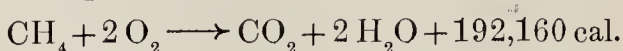


FIG. 147. Diagram of the miner's safety lamp

**Safety lamp.** Fortunately the kindling temperature of fire damp is high, and its flame may be extinguished by cooling. In 1815 Sir Humphry Davy (Fig. 76) invented a miner's lamp based on this principle, in which the usual chimney of a lantern is replaced by a wire gauze (Fig. 147). An explosion flame starting at the wick is so cooled by the metal wire that ignition ceases and the explosion is confined to the interior of the lamp. The principle may be demonstrated by holding a wire gauze a few inches above a Bunsen flame and parallel with the table (Fig. 148). When the gas is turned on and a light applied above the gauze, the resulting flame rests upon the gauze but does not pass through it to the burner.

**Halogen derivatives of methane.** As a rule the hydrogen present in a hydrocarbon may be displaced by a halogen element, atom for atom. In this way there are formed from methane a number of derivatives, the most important of which are the following :

*Chloroform* ( $\text{CHCl}_3$ ), a heavy, colorless liquid boiling at  $61.2^\circ$ , is the well-known anæsthetic used in surgery.

*Carbon tetrachloride* ( $\text{CCl}_4$ ) resembles chloroform in appearance. It is a good solvent, especially for fatty substances.

It is often used to remove grease spots

from fabrics. For this purpose it possesses the advantage over benzine of being noninflammable. Its chief use is as a fire extinguisher (p. 143). *Iodoform* ( $\text{CHI}_3$ ) is a yellow crystalline solid and is largely used as an antiseptic in the treatment of wounds.

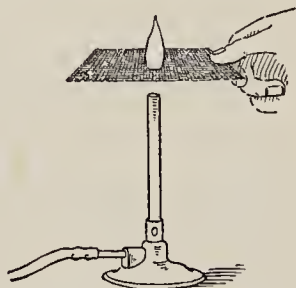


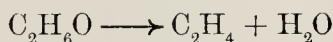
FIG. 148. An experiment to illustrate the principle of the safety lamp

**Ethane ( $C_2H_6$ ).** This hydrocarbon, a small quantity of which is present in coal gas, can be prepared from methane by first displacing an atom of hydrogen by one of chlorine and then treating the resulting compound with sodium:

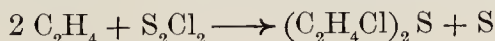


**Hydrocarbons of other series.** In addition to the methane series of hydrocarbons a number of other series are known, some of which include many members. Two of these hydrocarbons will be considered at this point, and several others will be referred to in subsequent pages.

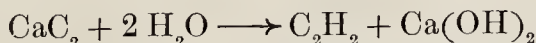
**Ethylene ( $C_2H_4$ ).** Ethylene is a colorless, highly inflammable gas, small percentages of which are present in coal gas. It is prepared by heating the vapor of ordinary alcohol ( $C_2H_6O$ ) in contact with kaolin (a compound of aluminum), which acts as a catalytic agent:



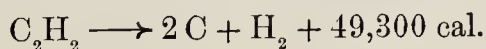
During the World War the United States prepared enormous quantities of ethylene for use in the manufacture of the poison liquid known as *mustard gas*. This compound, while called a gas during the war, is really a high-boiling, nearly colorless liquid. It has the formula  $(C_2H_4Cl)_2S$ , and its chemical name is *dichlorethyl sulfide*. It is absorbed by the skin, and after absorption it decomposes, forming hydrogen chloride, which produces large blisters and causes severe and often fatal inflammation. The compound is made by the action of ethylene on sulfur monochloride:



**Acetylene ( $C_2H_2$ ).** This hydrocarbon is a colorless gas having, when pure, a faint, pleasant odor. It is easily obtained by the action of water on calcium carbide ( $CaC_2$ ):



The gas is prepared in large quantities for use as an illuminant and as a source of intense heat. When heated it decomposes, with evolution of a great deal of heat:





By this method the Germans prepared much of the hydrogen used for filling the Zeppelins in the World War.

When compressed in cylinders, acetylene is very explosive, since the heat liberated in compressing the gas is sufficient to start decomposition. With the proper admixture of air it burns with a brilliant white light. The flame is very hot, because to

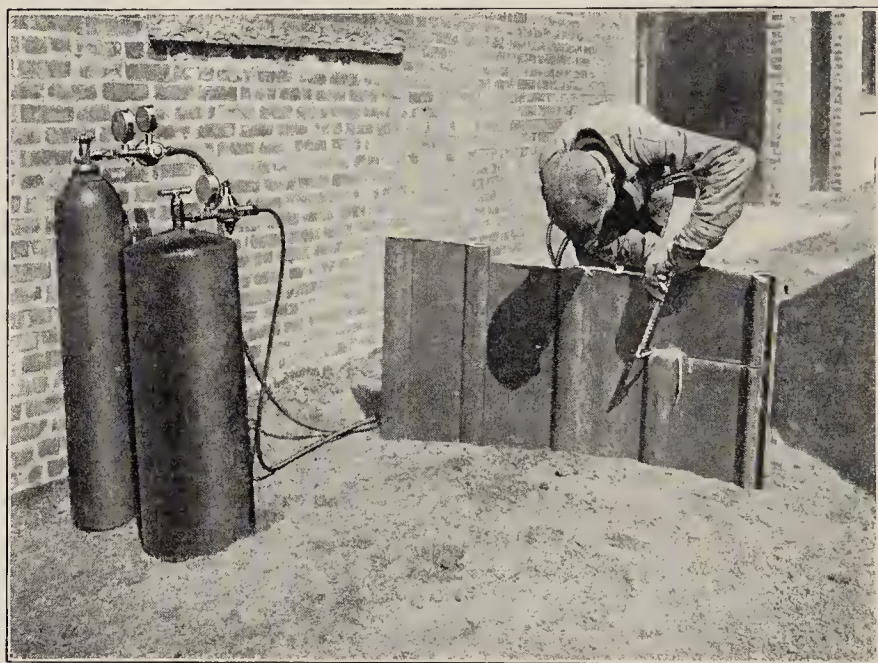
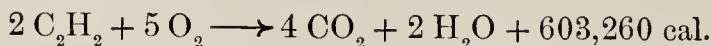


FIG. 149. Cutting an iron plate into pieces by the oxyacetylene blowpipe

the heat of combustion of the hydrogen and the carbon there is added the heat of decomposition of the acetylene undergoing combustion :



**Compression of acetylene.** It has been found that acetylene can be compressed with safety by forcing it at low temperatures into metal cylinders completely filled with some porous material, which has been partially saturated with certain liquids. For this purpose acetone, a liquid obtained by the destructive distillation of wood,

is often used. These liquids dissolve large volumes of the gas, and under such conditions it is not explosive. Stored in this way the gas is now a common article of commerce.

**Uses of acetylene.** As an illuminant, acetylene is often used in places where electric lights are not available. The chief use of the gas at present is in the cutting and welding of metals. For these purposes acetylene is burned in pure oxygen in a form of apparatus known as the *oxyacetylene blowpipe*, which is almost exactly like the oxyhydrogen blowpipe. A temperature of about  $2700^{\circ}$  may be obtained in this way. In dismantling iron structures the tip of the flame is held in contact with some part of the metal, until the metal is heated to a high temperature; additional oxygen is then turned on and the hot metal at once begins to burn away. By slowly moving the tip of the flame containing the excess of oxygen over the metal plate, the metal is cut into pieces (Fig. 149).

### EXERCISES

1. How could you distinguish between gasoline and kerosene?
2. Why not use kerosene as a fuel for motor cars?
3. Methane is formed by the decay of vegetable matter under water. What is the function of the water?
4. Write the equations for the combustion of the following hydrocarbons: (a) methane; (b) ethane; (c) acetylene.
5. Assuming that natural gas is pure methane, (a) how many liters of oxygen would be required to burn 1000 liters of the gas? (b) What volume of carbon dioxide would be produced? (See page 255 for simple method of solution.)
6. In what proportion by volume ought acetylene and oxygen to be mixed in an oxyacetylene blowpipe to get the maximum heat?
7. (a) Write the equation for the combustion of heptane. (b) Assuming that gasoline is pure heptane and that 1 gal. of it weighs 3500 g., what weight of oxygen would be required for the complete combustion of 1 gal. of gasoline? (c) What volume of air would be required to furnish this amount of oxygen?

8. On the supposition that calcium carbide costs 12 cents a kilogram, what would be the cost of an amount sufficient to generate 100 liters of acetylene measured at  $20^{\circ}$  and 740 mm.?

9. (a) How many calories of heat are evolved in the combustion of 100 liters of acetylene? (b) What weight of water at  $20^{\circ}$  would this heat convert into steam at  $100^{\circ}$ ?

10. The analysis of a certain compound showed it to have the following composition: carbon, 10.05%; hydrogen, 0.84%; chlorine, 89.10%. Its molecular weight was found to be approximately 120. Calculate the formula of the compound.

11. Calculate the volume of oxygen required to burn 1000 liters of acetylene; also the volume of the carbon dioxide formed.

12. Calculate the percentage composition of carbon tetrachloride.

## CHAPTER XXVIII

### FUELS; FLAMES: ELECTRIC FURNACES

**Fuels.** Many different substances are used as a source of heat through combustion. The most important of these are coal, wood, mineral oils, natural gas, and various manufactured fuel gases such as coal gas. While these fuels differ widely in their properties, they are all alike in that they are composed primarily of carbon and hydrogen, either in the free or in the combined state. The products of combustion of all these fuels, therefore, are chiefly carbon dioxide and water. Associated with these are varying quantities of other products such as free carbon, carbon monoxide, and sulfur dioxide. The sulfur dioxide is formed from traces of sulfur compounds which are present in almost all fuels.

**Ventilation.** Rooms are not infrequently heated by gas or oil stoves with no provision for removing the products of combustion. Likewise, natural gas is often burned in stoves or grates with the damper closed so as to leave no opening into the chimney. Such practices are greatly to be condemned, since the air in the rooms heated in this way soon becomes so contaminated with various products of combustion as to render it unfit for respiration and in some cases very poisonous (p. 252). The large amount of water vapor formed in rooms so heated condenses on the windows in cold weather, causing the glass to *sweat*.

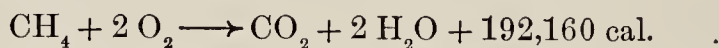
**The fuel gases.** A number of different kinds of gases are now used as a source of heat, light, and power. The most important of these are (1) natural gas, (2) coal gas, (3) water gas, and (4) producer gas. These will now be discussed in turn.

**Natural gas.** This is found stored in the earth in many localities, and, like petroleum, is obtained by boring wells into



the gas-bearing strata. It is generally associated with petroleum and is composed chiefly of methane, with small percentages of other hydrocarbons. The methane content averages about 85 per cent, although the gas from many fields contains as high as 95 per cent of methane. Nitrogen is generally present, but in very small quantities except in rare instances. Thus, the natural gas from the region of Fort Worth, Texas, contains as much as 38 per cent of nitrogen, the methane content falling to about 50 per cent. It is interesting to note that natural gas, which is rich in nitrogen, usually contains about 1 per cent of helium and serves as the source of helium used for inflating balloons (p. 92).

Natural gas is an ideal fuel and is often conducted through pipes for hundreds of miles from the gas fields to cities. It burns with a flame of moderate luminosity but works well with a gas mantle. It has a high heat of combustion, as shown in the following equation:



The natural gas from some wells contains a considerable percentage of the vapors of the hydrocarbons which constitute ordinary gasoline. When such a gas is passed through activated charcoal, these vapors are adsorbed. They are recovered by steam and constitute a high-grade gasoline known as *casing-head gasoline*. The annual production of gasoline from this source amounts to nearly 1,000,000,000 gal.

**Coal gas.** It has been known for several centuries that when soft, or bituminous, coal is heated out of contact with air, combustible gases are formed; indeed, gas obtained in this way was used for street lighting in London and Paris more than a hundred years ago.

**The manufacture of coal gas.** The manufacture of coal gas is represented in a diagrammatic way in Fig. 150. The coal is introduced into rows of closed retorts *A, A, A* and heated. A delivery pipe leads from the top of each of the retorts into a large pipe *B*



(known as the *hydraulic main*). The application of heat causes the coal to undergo complex changes which result in the formation of a large number of compounds. These compounds escape through the delivery pipe into the hydraulic main. The temperature being reduced, a small quantity of the products that are solid or liquid at ordinary temperatures condense in the hydraulic main in the form of a dark liquid mass known as *coal tar*. The gases then pass on into the condenser, in which the products are cooled to such an extent that the remaining tar is largely deposited. Along with the tar there is condensed a liquid (chiefly water) containing ammonia

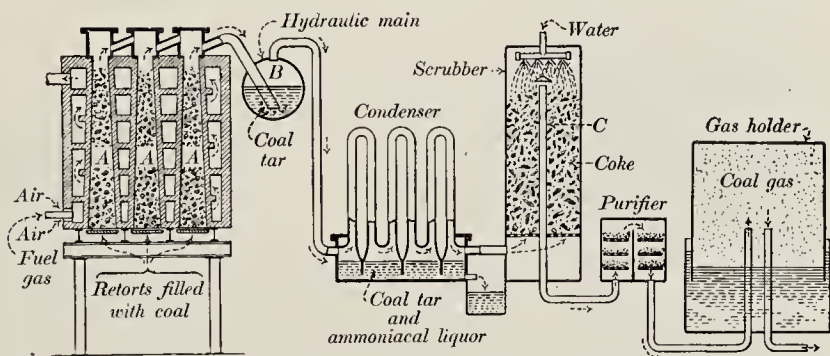


FIG. 150. Diagram showing the essential parts of the apparatus used in the manufacture of coal gas

in solution and known as *ammoniacal liquor*. The gas is then led into the scrubber, where it passes through a column of loose coke, over which water is sprayed. Here the gas is still further cooled and to some extent purified from soluble gases, such as hydrogen sulfide and ammonia. In some plants a second scrubber is used, in which the gas is washed with an oil which dissolves the small percentage of benzene (p. 407) present in the gas. The benzene so removed is recovered from the oil and used for making aniline and other products (p. 409). From the scrubber the gas passes down the pipe *C* into the purifier, where it comes in contact with lime or iron oxide, which removes the remainder of the sulfur compounds, and from this it enters the large gas holder, from which it is distributed to consumers.

The great bulk of the carbon remains in the retort as *coke* and as *retort carbon*. The yield of gas, tar, and soluble materials depends upon many factors, such as the composition of the coal,

the temperature employed, and the rate of heating. One ton of good gas coal yields approximately 10,000 cu. ft. of gas, 1400 lb. of coke, 120 lb. of tar, and 20 gal. of ammoniacal liquor.

Not only is the ammonia obtained in the manufacture of the gas of great importance, but the *coal tar is the source of many very useful substances*, as will be explained later.

**The by-product coke oven.** It will be observed that coke is formed in the process used in the manufacture of coal gas. Coke is a very

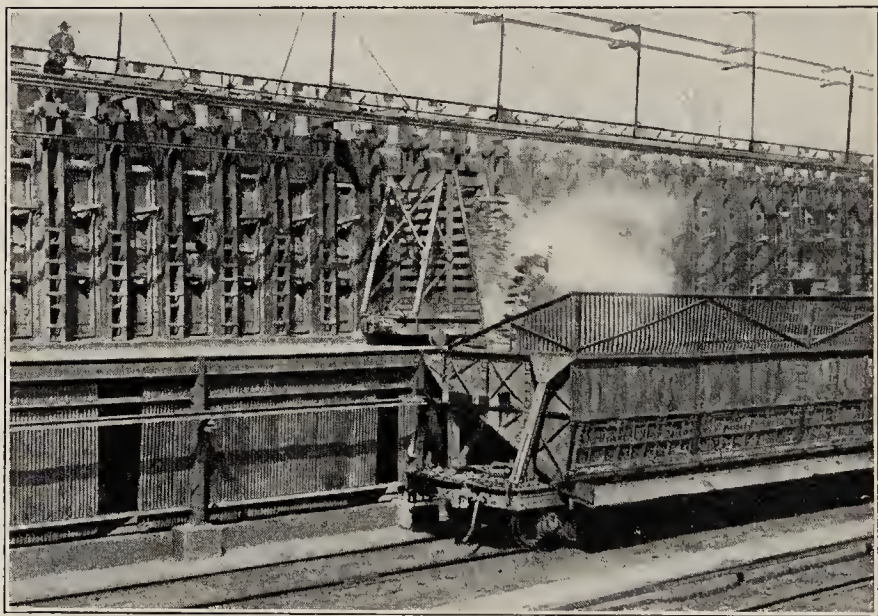


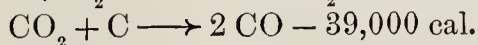
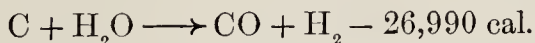
FIG. 151. View of a portion of a by-product coke oven

important product and is used in large quantities, especially in the reduction of metals, such as iron, from their ores. The quantity of coke obtained in the manufacture of coal gas has never been sufficient to meet the demand. Much of the additional coke required has been prepared by coking the coal in ovens called *beehive ovens* because of their shape. The coking of coal in these ovens is carried out as follows: The oven is nearly filled with coal, and the coal is ignited. After the fire is well started the draft is shut off, and the heat formed in the combustion of a portion of the coal is sufficient to coke the remainder of the coal. In this process all the coal tar, coal gas, and ammonia are lost.

The growing demand for ammonia, as well as for the products obtained from coal tar, has led to the construction of furnaces or ovens for the coking of coal which make it possible to save the coal tar and ammonia formed in the process. Such ovens are known as *by-product coke ovens*, this term being chosen because the ammonia and coal tar formed in the process of coking the coal are by-products, the coke being the main product. At the present time from 12 to 15 per cent of all the bituminous coal mined in the United States is used in the manufacture of coke. More than 75 per cent of this is coked in the by-product coke ovens.

Fig. 151 represents a portion of a large by-product coking plant. It consists primarily of a number of narrow, upright ovens placed side by side but separated sufficiently to admit of heating the coal with which the ovens are filled. As a rule a portion of the gas generated in the process is used as a fuel for coking the coal. The hot flame of the burning gas strikes against the bottom and sides of the ovens. The coal tar and ammonia are separated and collected as in the manufacture of coal gas; indeed, the by-product oven is a large coal-gas plant. When the process is complete, each oven is pushed forward and the coke dropped into a car as shown in the figure.

**Water gas.** Water gas is essentially a mixture of carbon monoxide and hydrogen. It is manufactured by passing superheated steam over very hot anthracite coal or coke, the chief reactions being expressed in the following equations:



Water gas has no odor, and as it is very poisonous, great care is required in its use.

**Industrial process.** The industrial process is intermittent. The fuel is burned with a forced draft in a suitable furnace until it is very hot. The air is then shut off and the steam turned on until the temperature falls to about 1000°. The process is then reversed. The fall in temperature is rapid, largely because of the endothermic character of the reactions which take place. The gas so formed contains all the nitrogen that was in the furnace when the steam was admitted.



**Enriching of water gas.** Water gas burns with a pale-blue, nonluminous flame. To make it suitable for illumination in an ordinary burner, as well as to give it an odor and so make it safer, it is enriched with hydrocarbons called illuminants. This is accomplished by passing the gas through a furnace filled with hot fire brick, piled in the form of checkerwork,

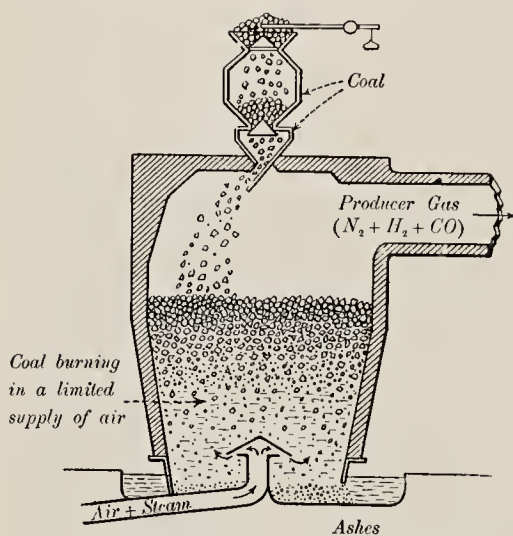


FIG. 152. Diagram illustrating the manufacture of producer gas

upon which a mineral oil is sprayed. The petroleum oils are decomposed (cracked) into simpler gaseous bodies, the most important of which are methane, acetylene, and ethylene.

**Producer gas.** Producer gas is used in connection with many metallurgical furnace operations and also as a fuel for gas engines. It is made by burning coal under such conditions

that the product of combustion is largely carbon monoxide (Fig. 152). Very often a little steam is admitted with the air, and this, on passing through the hot bed of coals, is reduced as in the preparation of water gas. Made in this way producer gas is composed mainly of carbon monoxide, hydrogen, and nitrogen. It can be made from coal of a poor quality, even from lignite; and as gas engines run well with this gas, it furnishes an economical method for utilizing low-grade coal for power.

**Comparative composition of gases.** The following figures are the results of analyses of average samples, but since each kind of gas varies considerably in composition, the values are to be taken as approximate only. The nitrogen and traces of oxygen are derived from the air.

COMPOSITION OF GASES EXPRESSED IN PERCENTAGE  
BY VOLUME

FORMULA OF THE CONSTITUENT GASES	OHIO NATURAL GAS	COAL GAS	WATER GAS	ENRICHED WATER GAS	PRODUCER GAS
H <sub>2</sub> . . . . .	0.0	41.3	52.88	37.96	10.90
CH <sub>4</sub> . . . . .	89.5	43.6	2.16	7.09	
C <sub>6</sub> H <sub>6</sub> . . . . .	9.3			2.01	
C <sub>2</sub> H <sub>2</sub> + C <sub>2</sub> H <sub>4</sub> . . . . .	0.3	3.9		9.40	0.60
CO . . . . .	0.4	6.4	36.80	32.25	20.10
CO <sub>2</sub> . . . . .	0.3	2.0	3.47	4.73	8.50
N <sub>2</sub> . . . . .	0.2	1.2	4.69	3.96	59.09
O <sub>2</sub> . . . . .	0.0	0.3		0.60	
Other hydrocarbons .		1.5		1.80	

**Relation of the two gases to the flame.** When a gas issuing from any kind of burner is ignited, the gas is said to undergo combustion, while the gas which constitutes the atmosphere about the flame is said to support combustion. These terms are entirely conventional, since the relation of the two gases may be reversed without greatly altering the appearance of the flame.

**Laboratory apparatus.** Fig. 153 illustrates a convenient apparatus for demonstrating this fact. A wide lamp chimney *A* is covered with a piece of asbestos board *B* which has a hole in the center about as large as a dime. A straight tube *C* about 1 cm. wide, and also a smaller tube *D* connected with the gas supply, pass through a cork at the bottom. If the hole in *B* is closed (by a piece of asbestos board) while gas is admitted through *D*, the excess gas escapes downward through *C*, where it may be lighted. If the hole in *B* is now opened, the flame will ascend to the top of the tube *C*. This flame is produced

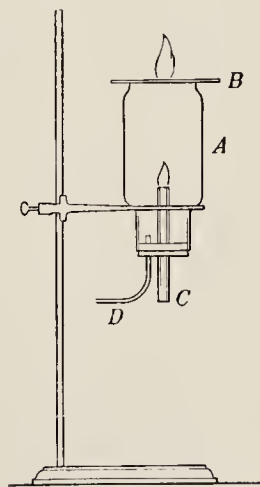


FIG. 153. Diagram of apparatus for showing the relation of two gases to the flame produced by their union



by air drawn up through *C*, burning in an atmosphere of coal gas. Finally, the excess of coal gas may be ignited at *B*, where it will burn in air, the two flames being very similar in their appearance.

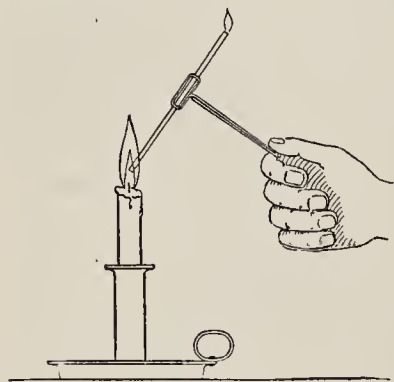


FIG. 154. An experiment to show that the interior of a candle flame contains combustible gases

or vapors at the temperature reached in the combustion, the act of union is accompanied by a *flame*.

**Flames from burning liquids or solids.** Many substances which are liquids or solids at ordinary temperatures burn with a flame because the heat of combustion slowly vaporizes them, and the flame is due to the union of this vapor with the oxygen of the air. This may be shown in the case of a candle flame by holding one end of a slender glass tube in the base of the flame (Fig. 154). The unburned vapor in the inner part of the flame is thus conducted away and may be ignited at the upper end of the tube.

**Bunsen burners.** In the ordinary Bunsen burner used in chemical laboratories the gas is mixed with a certain percentage of air before it is burned. This is accomplished by having an opening (mixer) (Fig. 155) in the base of the burner, into which the air is drawn by the flow of the gas. If the mixer is adjusted

### Conditions necessary for flames.

When one of the substances undergoing combustion remains solid at the temperature occasioned by the combustion, light may be given off, but there is no flame. Thus, iron wire burning in oxygen throws off a shower of sparks, but no flame is seen. When, however, both of the substances involved are gases

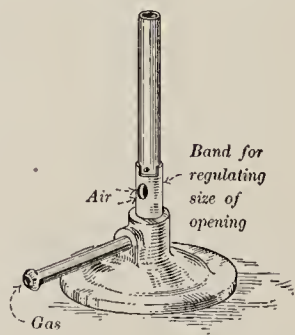


FIG. 155. Diagram of a Bunsen burner

so that the proper amount of air is admitted, the flame is colorless. Such a flame possesses an advantage in that it is very hot and no carbon is deposited from it.

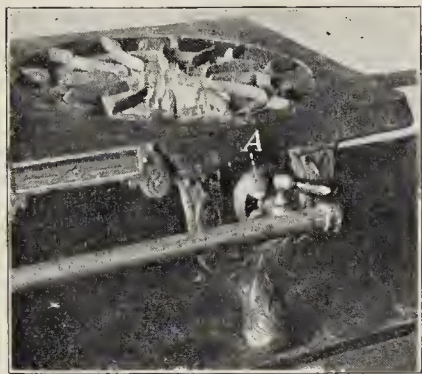


FIG. 156. View of a typical gas burner, showing mixer at *A*

All the burners used in gas ranges, as well as for illumination with the aid of gas mantles, are essentially Bunsen burners, although of various shapes. There is always some device (mixer) by means of which varying quantities of air may be mixed with the gas just before it issues from the burner (*A*, Fig. 156).

**Structure of a flame.** The structure of a flame can be studied to the best advantage when the combustible gas issues from a round tube into an atmosphere of the gas supporting combustion (usually the air), as is the case with an ordinary Bunsen burner. Under these conditions the flame is conical in outline.

**Simple flames.** When the chemical action taking place in combustion is the mere union of two gases, as is true in the union of hydrogen or carbon monoxide with oxygen, or of hydrogen with chlorine, the structure of the flame is very simple. It consists of two superimposed cones of different altitudes. The inner one may be shown to be merely unchanged cold gas, and is therefore not a real part of the flame. That the inner cone has a low temperature is shown by the fact that a match head suspended in this region (Fig. 157) before lighting the gas is not ignited by the flame around it.

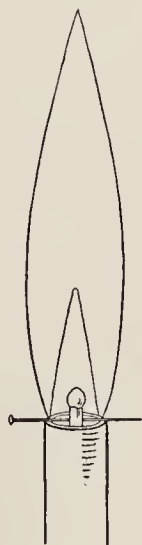


FIG. 157. Diagram of a simple flame

**Complex flames.** In the burning of hydrocarbons, as well as of many other gases, the flame is more complex, and as many as four distinct cones may be seen (Fig. 158). The

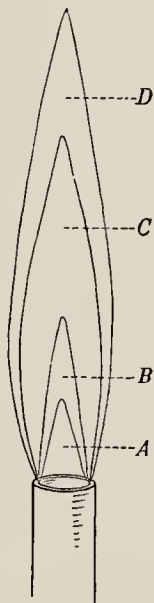


FIG. 158. Diagram of the cones of a complex flame

innermost one *A* is formed of gas not yet brought to the point of combustion. If a Bunsen burner is employed, with the ring at the base turned to admit plenty of air, the second cone *B* is sharply defined and is bluish green in color. If the burner tube is wide or too much air is admitted, the rate of combustion in this cone may exceed the rate of flow of the gas, and in this case cone *A* will disappear and the flame will travel down the tube and burn at the base, or *strike back*. As the air is shut off it will be seen that a luminous spot appears at the apex of cone *B*, which gradually takes the form of a cone *C*, quite covering the inner one and brightly luminous overall its surface.

Finally, if some object is held so as to intercept the light from this region, it will be seen that there is a fourth cone *D*, which is only faintly luminous.

In the candle flame (Fig. 159) there are, broadly speaking, three cones: (1) the inner cone *A*, composed of combustible vapors; (2) an intermediate cone *B*, in which these vapors are decomposed by the heat and carbon is set free, which renders the flame luminous; and (3) an almost invisible narrow outer cone, or film, *C*, in which the carbon and hydrogen are burned to water and carbon dioxide.

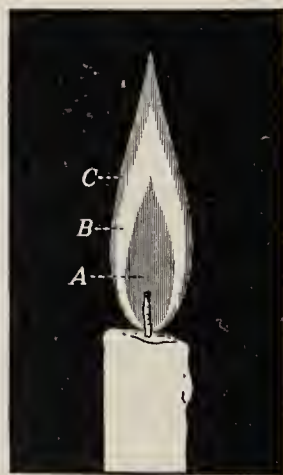
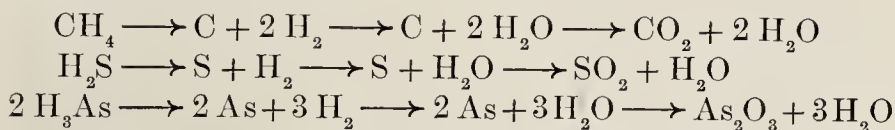


FIG. 159. Drawing showing the cones of a candle flame

**Luminosity of flames.** As the cold gas in the inner cone moves toward the hottest region of the flame its temperature rapidly rises, and at definite temperatures, which depend upon the nature of the gas, decomposition takes place. These decompositions cause sharp changes in the density of the gas, and this in turn makes the gas visible, just as air, heated by a hot pavement in summer, is visible in wavering lines. In this decomposition, products may be formed that are solids (such as carbon), and these become incandescent at the temperature reached, making the flame still more luminous. Each chemical change really produces a distinct cone in a steady flame. The luminosity of a flame thus depends upon many factors.

The following equations show some of the successive reactions that may take place in the combustion of the three different gases,  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ , and  $\text{H}_3\text{As}$ :



If we have a flame from any one of these burning gases and suddenly place a cold object (a small porcelain dish) in the flame, the free element is chilled below its kindling temperature and is deposited as soot (carbon, sulfur, arsenic) upon the dish.

**The temperature of flames.** The actual temperature which can be realized in an ordinary flame obviously depends upon many conditions, such as the composition of the gas, its pressure, temperature, and rate of flow, and the method of supplying the air. Even in an ordinary Bunsen flame burning under favorable conditions it is very difficult to determine the maximum temperature attained. The actual region of great heat is limited, as the burning zones are very thin. The temperature in different parts of the flame varies greatly, and any object placed in the flame for determining its temperature cuts across many different regions and is unequally heated. Evidently the temperature is much higher than that recorded by a body in the flame, since the specific heat of



solids is so much greater than that of gases. Under exceptional conditions it has been found possible to melt a very fine platinum wire in a good Bunsen flame so that a temperature of  $1755^{\circ}$  is surely reached. The accompanying diagram (Fig. 160) gives a rough estimate of the probable temperature in various parts of a good nonluminous Bunsen flame.

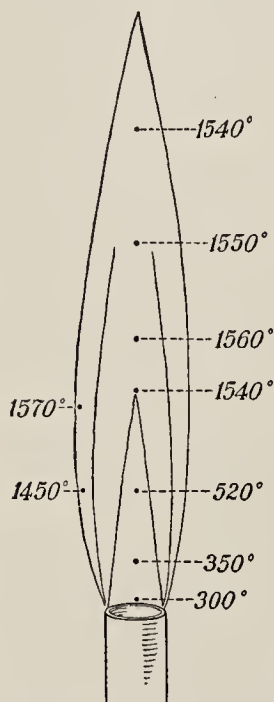


FIG. 160. An estimate of the temperature in various parts of a Bunsen flame

**Gas mantles.** In using natural gas or any of the fuel gases as illuminants the gas is usually mixed with air before burning. In this way the gas burns with a hot but nearly nonluminous flame. The light is obtained by suspending about this flame a gauze mantle of suitable material. The best mantles are composed of a mixture of 99 per cent of thorium oxide with 1 per cent of cerium oxide. The thorium and cerium compounds used in gas mantles are obtained from *monazite sand* (Fig. 161) found principally in Brazil.

**Manufacture of gas mantles.** The process of making a gas mantle consists in knitting a tubular fabric (Fig. 161), which is then dipped into a solution of the nitrates of thorium and cerium. After being dried the fabric is heated, and in this process the yarn is burned, while the nitrates of thorium and cerium are converted into oxides which are left in the form of the original fabric. The resulting mantle is very delicate and is strengthened for shipping by dipping it into a solution of an appropriate substance and drying.

**Reducing and oxidizing flames.** Since the region just below the luminous cone is very hot and contains the reducing gases hydrogen and carbon monoxide, a compound such as a metallic oxide placed in this region will undergo reduction, provided it can be reduced by such hot gases. A body heated in this

way is said to be heated in the *reducing flame*. At the apex of the flame there are no reducing gases, but it is very hot and air is abundant; consequently a substance which is rather readily oxidized will undergo oxidation if heated in this region. This part of the flame is called the *oxidizing flame*.

**Blowpipe tests.** In testing various substances it is sometimes desirable to try the effect of either the oxidizing or reducing flame upon the substance being tested. This is easily done by using a

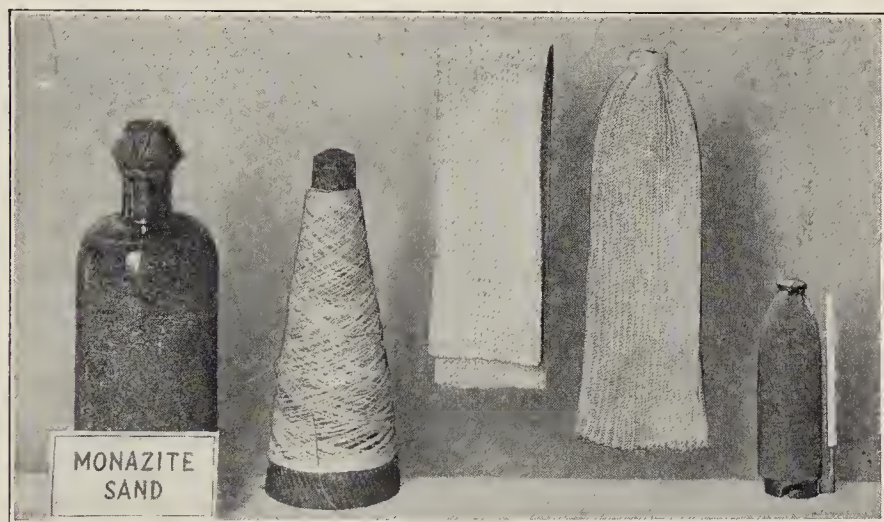


FIG. 161. Materials used in making gas mantles, and stages in the process of manufacture

mouth blowpipe, as shown in Fig. 162. The blowpipe is a metal tube bent at one end and drawn out to a fine point. When a current of air is forced through the tube, the end of which is placed just at the edge of a small Bunsen flame, as shown in the figure, the flame is bent at an angle. The tip of this flame is the oxidizing flame, while the interior is the reducing flame. The object to be heated is placed in a cavity on a piece of charcoal and held so that the desired flame strikes the object.

**Smoke prevention.** Since the products of combustion of fuels are carbon dioxide and water vapor, and these are invisible compounds, it is evident that if the combustion is

complete no smoke will be formed. As a rule the combustion is imperfect; gaseous compounds containing carbon are first formed, and when these are imperfectly burned a part of their carbon is set free in a finely divided colloidal state constituting smoke. Smoke may therefore be prevented by securing



FIG. 162. Heating a metal in the oxidizing flame

the complete combustion of the fuel, the necessary conditions being as follows: (1) a sufficient supply of air; (2) thorough mixing of the air with the combustible gases produced from the fuel; and (3) a temperature high enough to maintain active combustion.

**Practical details.** Smoke prevention is a problem of great economic importance, especially in the large cities. For example, the Citizens Advisory Smoke Abatement Commission of Chicago estimates the annual loss in Chicago due to smoke as \$42,500,000, and this does not take into account the possible effect of smoke upon health. Because of these facts many cities are now taking steps to abate the smoke nuisance. That the conditions necessary for preventing smoke may be met, it is essential that the coal be introduced into the furnace uniformly, so that the volatile matter expelled upon heating may be more readily mixed with air. This is done efficiently by having a chain grate, as is shown in *A* (Fig. 163). The coal is fed on this at *B*, and as the chain moves slowly forward the coal gradually enters the furnace; by the time it reaches the back part of the furnace *C* it is completely burned, the ashes falling out at *D*. The volatile matter expelled is thoroughly mixed with hot air led in through the back of the grate *E*, *E*.

**Calorific value of fuels.** The various materials used as fuels differ much in the heat which they give out when burned. While many other factors are concerned in the value of a fuel, the chief one is its heat of combustion. *The heat evolved by the combustion of one gram of a fuel is called its calorific value.* In large contracts the price paid for a fuel is generally based

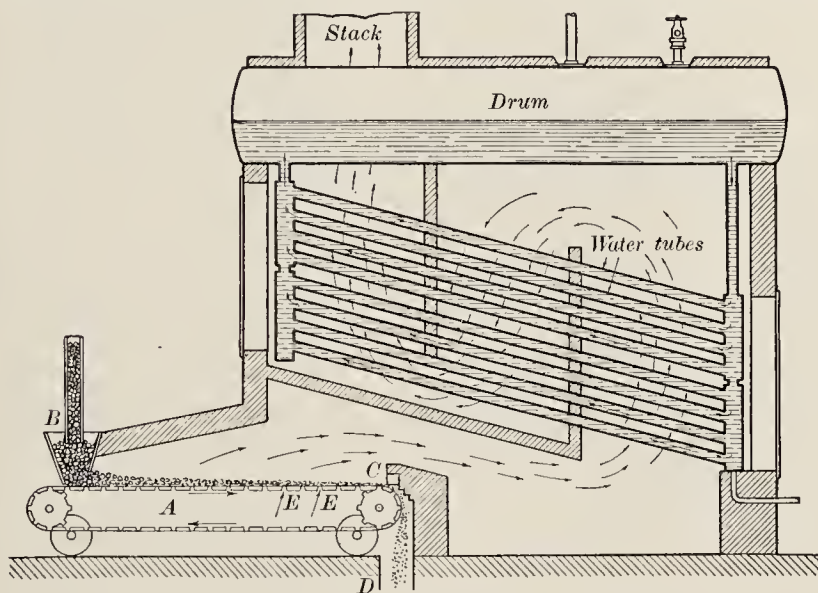


FIG. 163. Diagram of a smoke-consuming furnace

on its calorific value, as well as upon its adaptability to the use to which it is to be put. The following table will give some roughly approximate values for a few common fuels:

#### CALORIFIC VALUE OF FUELS

Wood (air-dried) . . . . .	about 3800-4000 cal.
Lignite (brown), 8% ash, 12% moisture . . .	about 5400 cal.
Bituminous coal (Pennsylvania), 35% volatile matter, 6% ash . . . . .	about 8300 cal.
Bituminous coal (Pocahontas), 18% volatile matter, 6% ash . . . . .	about 8700 cal.
Anthracite, 12% ash . . . . .	about 7300 cal.
Coke, 10% ash . . . . .	about 7300 cal.



**The bomb calorimeter.** In determining the calorific value of a fuel an instrument known as a *bomb calorimeter* is used. This is a strong steel flask lined with platinum or porcelain and provided with a tight-fitting screw cap (Fig. 164). In determining the heat of combustion a weighed sample of the substance is placed on the capsule

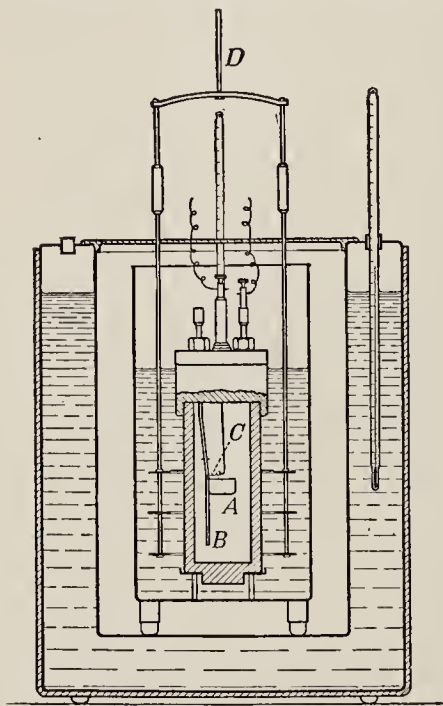


FIG. 164. Diagram of a bomb calorimeter

*A*, oxygen is admitted through the tube *B* until the pressure in the bomb is about 20 atmospheres, and the bomb is then closed and placed in an open calorimeter. The charge is ignited by passing an electric current through the fine iron fuse-wire *C* stretched above the charge. The wire is melted, and the red-hot drop of burning metal falls upon the charge, igniting it. The heat given off during combustion is measured by the rise in temperature of the water which surrounds the bomb, and which is stirred by the stirrer *D*. A preliminary experiment must be made upon a weighed charge of a substance whose heat of combustion is known (such as cane sugar), to determine the

heat absorbed by the bomb, together with that due to the melting and combustion of the fuse-wire and also the loss by radiation.

**The electric furnace.** In recent years electric furnaces have come into wide use in operations requiring a very high temperature. Temperatures as high as  $3500^{\circ}$  can easily be reached, whereas the hottest oxyhydrogen flame is not much above  $2000^{\circ}$ . These furnaces are constructed on one of two general principles.

1. **Arc furnaces.** In the one type the source of heat is an electric arc formed between carbon electrodes separated a little from each other, as shown in Fig. 165. The substance to be heated is placed in a vessel, usually a graphite crucible, just below the arc. The

electrodes and crucible are surrounded by materials which fuse with great difficulty, such as magnesium oxide, the walls of the furnace being so shaped as to reflect the heat downward upon the contents of the crucible.



FIG. 165. Diagram of an arc furnace

**2. Resistance furnaces.** In the other type of furnace the heat is generated by the resistance offered to the current in its passage through the furnace. In its simplest form it may be represented by Fig. 166. The furnace is merely a rectangular box built up of loose bricks. The electrodes

$E, E$ , each consisting of a bundle of carbon rods, are introduced through the sides of the furnace. The materials to be heated  $C$  are filled into the furnace up to the electrodes, and a layer of broken coke is arranged so as to extend from one electrode to the other. More of the charge is then placed on top of the coke. In passing through the broken coke the electrical current encounters great resistance. This generates much heat, and the charge surrounding the coke is brought to a very high temperature. The advantage of this type of furnace is that the temperature can be regulated to any desired intensity.

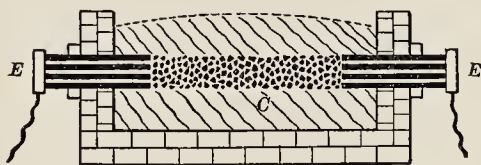


FIG. 166. Diagram of a resistance furnace

### EXERCISES

1. Why does charcoal usually burn with no flame? How do you account for the flame sometimes observed when it burns?
2. How do you account for the fact that a candle burns with a flame?
3. What two properties must the mantle used in the Welsbach lamp possess?
4. Would anthracite be suitable for the manufacture of coal gas?
5. How could you prove the formation of carbon dioxide and water in the combustion of illuminating gases?
6. Suggest a probable way in which natural gas has been formed.

7. Calculate the relative volumes of the carbon monoxide and hydrogen formed according to the equation  $C + H_2O \longrightarrow CO + H_2$ . Compare your results with the composition of water gas as given in the table on page 381. Account for the difference.

8. A room  $5 \times 6 \times 3$  meters is heated by a portable gas stove burning 10 cu. ft. of gas per hour. (a) If the gas consumed is pure methane, what weight of combustion products are formed in five hours? (b) What will be the volume of the carbon dioxide formed at  $20^\circ$  and 740 mm.? (c) How will this compare with the volume present in normal air in a room of the above dimensions?

9. (a) How many liters of oxygen will 100 liters of methane require for its combustion? (b) Contrast the volumes of the methane and oxygen with the volumes of the products formed, all being measured under the same conditions of temperature and pressure. (c) Why does an explosion of natural gas shatter a building?

## CHAPTER XXIX

### CARBOHYDRATES; ALCOHOLS; COAL-TAR COMPOUNDS

**Carbohydrates.** The term *carbohydrate* is applied to a class of compounds which includes the sugars, starch, and allied substances. These compounds contain carbon, hydrogen, and oxygen, the last two elements usually being present in the proportion in which they combine to form water. The most important carbohydrates are the following:

TABLE OF CARBOHYDRATES

Sucrose (ordinary sugar) . . . . .	$C_{12}H_{22}O_{11}$
Lactose (milk sugar) . . . . .	$C_{12}H_{22}O_{11} \cdot H_2O$
Maltose (malt sugar) . . . . .	$C_{12}H_{22}O_{11} \cdot H_2O$
Dextrose (grape sugar) . . . . .	$C_6H_{12}O_6$
Levulose . . . . .	$C_6H_{12}O_6$
Cellulose . . . . .	$(C_6H_{10}O_5)_x$
Starch . . . . .	$(C_6H_{10}O_5)_x$

The molecular formulas of cellulose and starch are unknown but are multiples of the simple formula  $C_6H_{10}O_5$ ; accordingly they are often written  $(C_6H_{10}O_5)_x$ . In the discussion of the compounds they will be represented by the simple formula  $C_6H_{10}O_5$ .

**Isomeric compounds.** It will be noted that some of the compounds named in the table have identical formulas. *Compounds that have the same empirical formulas are said to be isomeric.* Thus, dextrose and levulose are isomeric compounds. The difference in the properties of isomeric compounds is due to the fact that the atoms are arranged differently in the molecule. Just as two houses may be entirely different and yet be built from the same kind and the same number of



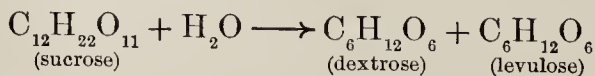
bricks, so two compounds may be different and yet the molecules of each may contain the same elements and the same number of atoms of each.

**Sucrose (sugar) ( $C_{12}H_{22}O_{11}$ ).** A great many different sugars are known. Sucrose, or ordinary *sugar*, is the most common of these. This compound occurs in many plants, especially in the sugar cane and sugar beet. The sugar cane grows only in warm climates (Cuba and the Hawaiian Islands are the greatest producers), while the sugar beet thrives in cooler climates, such as prevail in Ohio and Michigan in the United States, and in Germany. The beets contain as high as 20 per cent of sucrose. At present the sugar cane furnishes much more than half the world's supply of sugar.

It should be kept in mind that *cane sugar* and *beet sugar* are identical, and not even the trained chemist can tell the source of a sample of *pure* sugar.

**The manufacture of sugar.** The juice from the cane or beet contains the sugar in solution along with many impurities. These impurities are removed by appropriate methods, and the resulting solution is then evaporated until the sugar crystallizes. The evaporation is conducted in closed vessels from which the air is partly exhausted (vacuum pans). In this way the boiling point of the solution is lowered and the charring of the sugar is prevented. It is not practicable to remove all the sugar from the solution. Ordinary *molasses* is the solution which remains after a part of the sugar has been crystallized out from the purified juice of the sugar cane. The sweetness of maple sugar is due to sucrose, other products present in the maple sap imparting the distinctive flavor. The annual consumption of sugar in the United States amounts to about 100 lb. for each person.

**Chemical conduct of sugar.** When a solution of cane sugar is heated to about  $70^\circ$  with water and hydrochloric acid, two isomeric sugars, *dextrose* and *levulose*, are formed in accordance with the following equation:



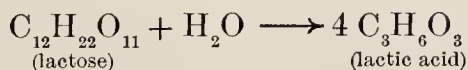
In this process the sugar is said to be *inverted*, and the mixture of dextrose and levulose is termed *invert sugar*.

When heated to  $186^{\circ}$ , sucrose melts; if the temperature is increased to about  $215^{\circ}$ , a partial decomposition takes place and a brown substance known as *caramel* is formed. This is used extensively as a coloring matter and in making confectionery.

**Lactose (milk sugar)** ( $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{H}_2\text{O}$ ). This compound is present in the milk of all mammals. The average composition of cow's milk is as follows:

Water . . . . .	87.17%
Casein (nitrogenous matter) . . . . .	3.56%
Butter fat . . . . .	3.64%
Lactose . . . . .	4.88%
Mineral matter . . . . .	0.75%

When *rennin* (a substance obtained from the stomach of calves) is added to milk, the casein coagulates. This is the part of the milk used in the manufacture of *cheese*. The liquid remaining after the separation of the casein is known as *whey*. This contains the milk sugar, which crystallizes on evaporation; it resembles sucrose in appearance, but is not as sweet or as soluble. The souring of milk is due to the fact that the milk sugar contained in it changes into *lactic acid*, a liquid having the formula  $\text{C}_3\text{H}_6\text{O}_3$ :

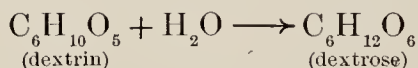


This change is brought about by a certain microörganism which enters from the air, and the process is known as *lactic fermentation*.

**Maltose (malt sugar)** ( $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{H}_2\text{O}$ ). This sugar resembles sucrose and lactose in its general properties. It is prepared by the action of malt upon starch; hence the name *maltose*. Malt is the name applied to barley which has been moistened, kept in a warm place until it has germinated, and then heated

until the vitality of the grain has been destroyed. In the process of germination a substance is formed known as *diastase*, and it is this substance which imparts to malt its property of changing starch into maltose.

**Dextrose (grape sugar, glucose) ( $C_6H_{12}O_6$ ).** This sugar is present in honey and in many fruits. It is usually associated with levulose, and is often called *grape sugar* because of its presence in grape juice. It can be obtained along with levulose by heating sucrose with hydrochloric acid, as explained above. Commercially it is prepared in enormous quantities by heating starch with hydrochloric acid. The starch is first changed into a sweet-tasting solid known as *dextrin*, and this, on further action, is converted into dextrose:



When the change is complete the hydrochloric acid is neutralized by sodium carbonate. Over 50,000,000 bushels of corn are used each year in the United States in the production of dextrose and allied products.

Pure dextrose is a white crystalline solid resembling sucrose in its properties, but not so sweet. Most of the dextrose used is in the form known commercially as *glucose* or *corn sirup*. This is a thick, sirupy liquid and consists of an aqueous solution of dextrin, dextrose, and maltose. Large quantities of glucose are used in the preparation of jellies, jams, sirups, candy, and other sweets. A federal ruling requires that when glucose is present in such foods as jellies and jams the label on the container must state the percentage of glucose present.

**Starch ( $C_6H_{10}O_5$ ).** This substance is always present in seeds and tubers and is by far the most abundant carbohydrate found in nature. In the United States it is obtained chiefly from corn, about 60 per cent of which is starch. In Europe the potato serves as the principal source.

**The manufacture of starch.** In manufacturing starch from corn the corn is first soaked in water containing a little sulfurous acid, to soften the grain. It is then ground coarsely so as not to crush the germ. When the resulting mass is mixed with water the germ floats, being very light because of the oil which it contains. In this way the germ is separated from the rest of the seed, and from it *corn oil* is prepared. The remaining material, consisting of the starch, the nitrogenous constituent (gluten), and the bran, or outside coating of the grain, is then ground fine, mixed with

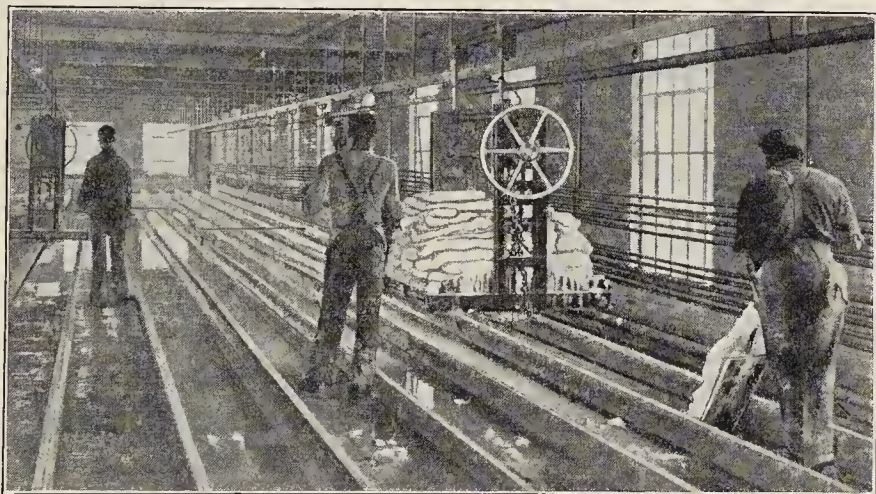


FIG. 167. Removing the starch from the settling troughs in a starch factory

water, and passed through cloth sieves, which remove the bran. The water containing the starch and gluten in suspension is then allowed to run slowly down long, shallow troughs, the rate of flow being so regulated that the heavier starch sinks to the bottom of the trough, while the lighter gluten is washed away. The starch is then removed from the troughs as shown in Fig. 167, and subsequently dried. Large quantities of starch are used in making glucose and other foods, for finishing cloth, and for laundry purposes.

**Characteristics of starch.** Starch consists of minute granules which differ somewhat in appearance according to the source of the starch, so that it is often possible from a microscopic examination to determine from what plant any given sample



of starch was obtained (Fig. 168). When heated with water the granules burst and the starch partly dissolves. This is the reason why starchy foods are made more digestible by cooking.

**Cellulose ( $C_6H_{10}O_5$ ).** Cellulose is the basis of all wood fibers. Cotton and linen are nearly pure cellulose. Cellulose is insoluble in water and dilute acids, but dissolves in a solution

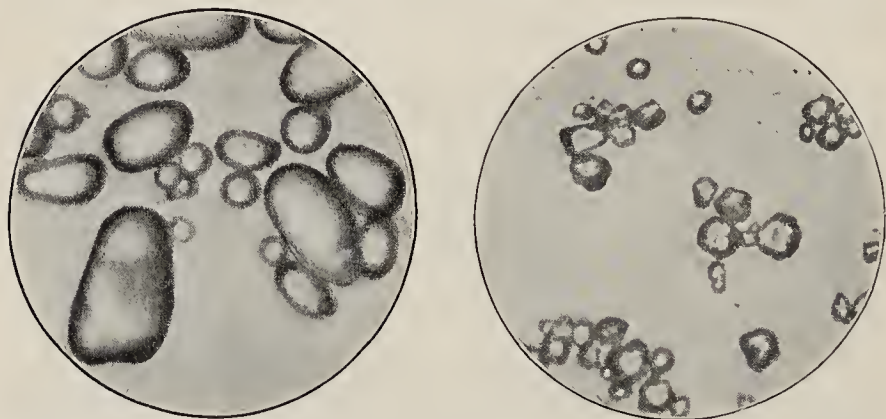
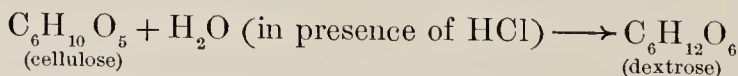


FIG. 168. View of granules of wheat starch (at left) and of corn starch (at right). Magnified 290 diameters

prepared by dissolving copper oxide in ammonium hydroxide. Concentrated hydrochloric acid changes it into dextrose:



A mixture of sulfuric and nitric acids acting upon it forms a number of compounds collectively known as *nitrocellulose* or *guncotton*. In these compounds a part of the hydrogen and oxygen of the cellulose has been displaced by the radical  $NO_2$ , so that they are really *nitrates*. They are white solids but can also be obtained in transparent form. They are inflammable and under certain conditions highly explosive.

**The uses of nitrocellulose.** Nitrocellulose has many uses, the most important of which are as follows: (a) It is the chief constituent of *smokeless powders* (p. 457). (b) *Photographic films*

are made from nitrocellulose, as well as from a derivative known as cellulose acetate, which is not so inflammable as nitrocellulose. (c) *Artificial leather* and some grades of *artificial silk* are made from nitrocellulose. (d) *Collodion* is a solution of nitrocellulose in a mixture of alcohol and ether. When this solution is placed on the skin the heat of the body soon evaporates the solvents and the nitrocellulose is deposited in a closely adhering film; hence collodion is sometimes used as a covering for wounds in place of court plaster. (e) *Celluloid* is a mixture of nitrocellulose and camphor (a white solid obtained from the camphor tree, which grows in Japan). These two, when mixed together, form a plastic mass which can be molded into any desired shape and when hard is used for making such objects as combs and brush handles. While the natural color of celluloid is white, it is often tinted with dyes and can also be obtained in transparent form. For example, the "flexible glass" used in automobile curtains is transparent celluloid. Because of the nitrocellulose present, celluloid is inflammable and should not be brought near a hot flame. (f) Nitrocellulose dissolved in a suitable solvent constitutes the base of the modern *lacquers* (p. 577).

**Mercerized cotton and rayon (artificial silk).** When cotton cloth is treated with a concentrated solution of sodium hydroxide, the cellulose shrinks and becomes tougher. If the cloth is placed in stretchers to prevent the shrinkage, it assumes an appearance somewhat resembling silk and is known as *mercerized cotton*. Another fabric prepared in large quantities from cellulose resembles silk very closely and is known as *rayon*. The fiber of this fabric is prepared by forcing concentrated solutions of cellulose or its derivatives through minute tubes and coagulating the cellulose as it emerges in the form of fine threads.

**Characteristics of various textile fibers.** Of the different fibers used in making the yarns from which the common fabrics are prepared, the vegetable fibers, cotton and linen, are essentially cellulose, while the animal fibers, wool and silk, are composed of nitrogenous substances. Although these fibers resemble each other when viewed with the naked eye, their appearance is distinctive when examined with the microscope. The characteristic appearance of these fibers is shown in

Fig. 169. It is also possible to distinguish between the fibers by the action of chemical reagents. For example, a hot solution of sodium hydroxide containing from 5 per cent to 10 per cent of the hydroxide has but little action upon cotton, while it will readily dissolve wool and slowly dissolve silk.

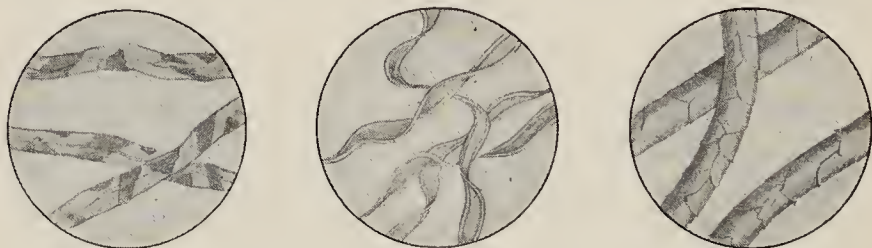


FIG. 169. Microscopic appearance of three important textile fibers  
Left, silk fiber; center, cotton fiber; right, wool fiber

**Paper.** Paper consists mainly of cellulose. The finer grades of paper are made from linen and cotton rags and the cheaper grades chiefly from wood.

**Manufacture of paper.** In making paper the raw material is cut into pieces and treated with suitable reagents (either calcium acid sulfite or sodium hydroxide is used in case of wood), to remove all objectionable matter, leaving the cellulose, which is then bleached

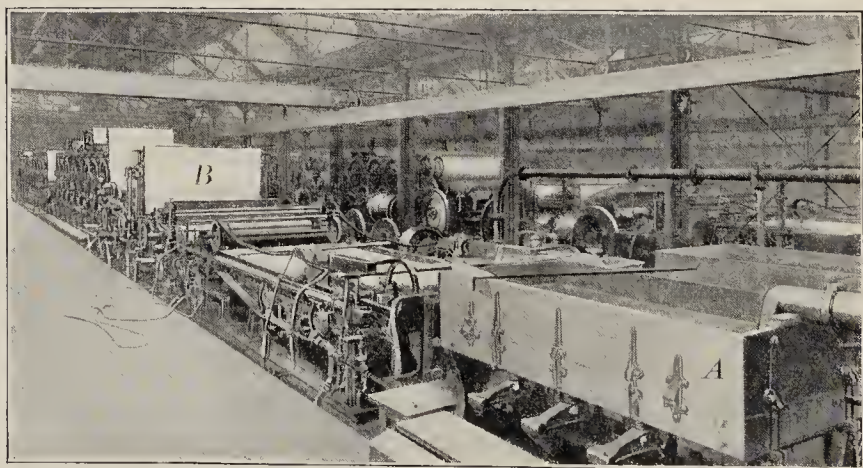


FIG. 170. View of the interior of a paper mill

with chlorine. The paper pulp so obtained is suspended in water and run onto wire screens. It then passes between large iron cylinders, some of which are heated with steam. In this way the pulp is pressed and dried and delivered in the form of paper. In the process different materials are often added to the pulp. These vary with the nature of the paper desired; thus, finely ground clay or calcium sulfate is added to give body to the paper. In making paper intended for writing or printing, a compound prepared by heating resin and sodium hydroxide is added, together with aluminum sulfate. This makes a finished surface and prevents the ink from spreading.

Fig. 170 shows the interior of a paper mill. The pulp flows from the container *A* onto the screens beyond and then between the rollers until it is pressed and dried and so converted into the finished paper *B*.

## ALCOHOLS

**Kinds of alcohols.** The alcohols may be regarded as derived from the hydrocarbons by substituting for one or more hydrogen atoms a corresponding number of hydroxyl groups. A great many alcohols are known, and, like the hydrocarbons, they may be arranged in series. The relation between the first three members of the methane series of hydrocarbons and the corresponding alcohols is shown in the following table:

$\text{CH}_4$ (methane)	. . . . .	$\text{CH}_3\text{OH}$ (methanol, methyl alcohol)
$\text{C}_2\text{H}_6$ (ethane)	. . . . .	$\text{C}_2\text{H}_5\text{OH}$ (ethyl alcohol)
$\text{C}_3\text{H}_8$ (propane)	. . . . .	$\text{C}_3\text{H}_7\text{OH}$ (propyl alcohol)

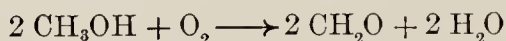
The terms *methyl*, *ethyl*, and *propyl*, used in designating the different alcohols, are names applied to the univalent radicals  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , and  $\text{C}_3\text{H}_7$  respectively. It will be noted that the names of these radicals are derived from the names of the corresponding hydrocarbons by changing the ending *-ane* to *-yl*.

**Methanol (wood alcohol) ( $\text{CH}_3\text{OH}$ ).** This compound is formed when hard wood is heated in the absence of air (p. 136), and on this account it is often called *wood alcohol*. It is a colorless liquid which boils at  $64.5^\circ$  and burns with an almost colorless



flame. It is a good solvent for organic substances and is used extensively for this purpose. *Wood alcohol is poisonous*, and many deaths have resulted from using it as an intoxicant. It also has a specific action on the optic nerve, and many persons have become blind from drinking the liquid or from repeatedly inhaling its vapor. Duncan states that "out of ten men who drink 4 oz. of pure methyl alcohol in any form whatever, four will probably die, two of them becoming blind before death. The remaining six may recover, but of these, two will probably be permanently blind."

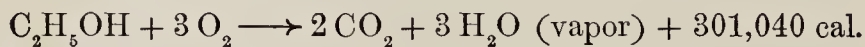
**Formaldehyde ( $\text{CH}_2\text{O}$ ).** When a mixture of the vapor of methyl alcohol and air is passed over hot copper, the alcohol is oxidized and a gaseous compound known as *formaldehyde* is formed:



This gas is now prepared in large quantities and used as a disinfectant. A 40 per cent aqueous solution of it is sold under the name of *formalin*.

**Ethyl alcohol (grain alcohol, alcohol) ( $\text{C}_2\text{H}_5\text{OH}$ ).** This compound is the one ordinarily known as *alcohol*. It resembles methyl alcohol in its general properties but is not so poisonous.

1. **Properties.** Ethyl alcohol is a colorless liquid with a pleasant odor different from that of methanol. It has a density of 0.789 at  $20^\circ$ , boils at  $78.5^\circ$ , and solidifies at  $-117.3^\circ$ . When ignited it burns with a hot flame:



It is sometimes used as a source of heat, since it does not deposit carbon, as does the flame from oils. When taken into the system in small quantities it causes intoxication; in larger quantities it acts as a poison. The intoxicating properties of such liquors as beer, wine, and whisky are due to the alcohol present.

2. **Preparation.** Ethyl alcohol is prepared by the action of ordinary brewers' yeast upon certain sugars, especially maltose and dextrose. With dextrose the reaction is expressed by the following equation:



This process, in which a sugar is changed into alcohol and carbon dioxide by the action of yeast, is known as *alcoholic fermentation*. The yeast is a low form of plant life (Fig. 171) which grows in the sugar solution under suitable conditions. During its growth it secretes a substance known as *zymase*, which is the active agent in effecting alcoholic fermentation. While sucrose does not ferment directly, the addition of yeast to its aqueous solution first resolves the sucrose into dextrose and levulose, both of which then ferment. Alcohol may also be prepared from starch. The starch is first converted into the sugar maltose by the action of malt (p. 395). Yeast is then added and the maltose ferments. Nearly all the alcohol made for commercial use in the United States is prepared by the fermentation of the sugar in crude molasses. The molasses is shipped from Cuba in large quantities and used for this purpose.

If sufficient sugar is present, it is possible to obtain by direct fermentation an aqueous solution containing from 15 to 20 per cent of alcohol. By fractional distillation this may be concentrated to a solution containing 96 per cent of alcohol. When lime ( $\text{CaO}$ ) is added to this solution, and the mixture heated, most of the remaining water combines with the lime to form calcium hydroxide. Upon distilling the resulting mixture, alcohol containing less than 1 per cent of water distills



FIG. 171. Appearance of some cells of the yeast plant when viewed under the microscope

over. This product is termed *absolute alcohol*. The ordinary alcohol of the druggist contains approximately 95 per cent by volume of alcohol and 5 per cent of water.

**Alcoholic liquors.** All alcoholic liquors are made by alcoholic fermentation. Wine is made by the fermentation of the dextrose in grape juice and contains from 5 to 15 per cent by volume of alcohol. Beer is made from maltose, formed by the action of malt upon starch obtained from various grains, chiefly barley. It contains from 3 to 5 per cent by volume of alcohol. Whisky contains about 50 per cent by volume of alcohol and is made from starch by a process very similar to that described under the commercial preparation of alcohol. Almost any saccharine liquid, such as cider and the juices of fruits in general, gradually undergoes alcoholic fermentation when exposed to air, the yeast cells entering from the air.

**The taxing of alcohol and alcoholic liquors; denatured alcohol.** From very ancient times men of all nations have prepared alcoholic liquors of various kinds as beverages. In alcoholic content these range from 3 and 5 per cent, in beers and light wines, to 50 per cent and higher, in whiskies and brandy. Governments have found these beverages to be a fruitful source of revenue and have imposed heavy taxes on all kinds of alcoholic liquors, carefully supervising their manufacture. They have also taxed pure alcohol heavily because imitation beverages can very easily be made from it. The amount of the tax on the pure alcohol varies with the percentage of alcohol present. This tax is imposed on the basis of what is known as a *proof gallon*, that is, a gallon containing 50 per cent by volume of alcohol, and amounts to \$1.10 per proof gallon. This amounts to a tax of \$2.10 on the ordinary 95 per cent alcohol. Even with this tax, the Federal law prohibits the sale of pure alcohol to only a few uses, chiefly medicinal.

The high tax on alcohol and alcoholic liquors has been justified on the ground that alcohol as a beverage is a luxury,

the use of which should be discouraged. This reason, however, ignores the fact that pure alcohol has many important industrial uses, and no nation desires to impede legitimate industrial progress. In order not to discourage the use of alcohol for industrial purposes, and at the same time to prevent alcohol sold for industrial purposes from being used as a beverage, the Federal government allows *denatured alcohol* to be sold tax free for commercial purposes. Denatured alcohol is alcohol to which has been added a definite amount of some substance which renders it unfit for beverage purposes but which does not impair its use for manufacturing purposes. The substances which may be used for this purpose are prescribed by law and are known as *denaturants*. The most common denaturants are (1) the two vile-smelling products known as alcotate and aldehyol, obtained from crude petroleum, (2) methanol (wood alcohol), (3) benzine. The pure alcohol when used for scientific purposes can be obtained, tax free, by educational institutions.

**Chemical changes in bread-making.** The average composition of wheat flour is as follows:

Water . . . . .	11.9%
Protein (nitrogenous matter) . . . . .	13.3%
Fats . . . . .	1.5%
Starch . . . . .	72.7%
Mineral matter . . . . .	0.6%

In making bread, flour is mixed with water, yeast, salt, and a little sugar, and the resulting dough is set aside in a warm place for a few hours. The yeast first causes the sugar to undergo alcoholic fermentation. The carbon dioxide formed escapes through the dough, making it light and porous. The yeast plant thrives best at about 30°; hence the necessity for keeping the dough in a warm place. In baking bread the heat expels the alcohol and also expands the bubbles of carbon dioxide caught in the dough, causing it to become porous and making the bread light.



**Preservatives.** We have observed that the changes taking place in the souring of milk and the changing of sugar into alcohol are caused by microorganisms the spores of which are present in the air. Many other similar changes, such as putrefaction, are due to the same causes. All these changes may be prevented in one of the following ways :

1. The substance may be kept at such a low temperature that the organism causing the change cannot thrive (cold storage).

2. The substance may be heated so as to destroy all organisms present, and may then be sealed air-tight in a suitable container. This is the method used in canning vegetables and in preserving such substances as grape juice and condensed milk.

3. Some substance may be added which in small quantities will destroy the organisms causing the change or will prevent their growth. Such a substance is known as a *preservative*.

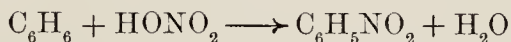
Whether or not preservatives should be permitted in foods is a much-debated question. Some people maintain that any substance which is powerful enough to prevent the growth of the organisms must have an injurious action upon digestion. The Federal government at present allows the use of *sodium benzoate* (a white solid made from a hydrocarbon present in coal tar) in such foods as jellies, jams, and catchup, which are not consumed immediately upon the opening of the container. If this preservative is used, however, the labels on the containers must state the amount present.

## THE COAL-TAR COMPOUNDS

**Coal tar and the coal-tar compounds.** In the discussion of the manufacture of coal gas (p. 376) we learned that along with the gas, coke, and ammonia there is formed a thick, tarry liquid known as *coal tar*. This liquid is composed of a mixture of a large number of compounds and serves as the commercial source of some eight or ten important ones. These are obtained from the coal tar by fractional distillation in a manner entirely analogous to that used in refining petroleum. Moreover, each of the compounds so obtained serves as the source material from which many other useful compounds are prepared. *There are many thousands of these compounds, and all*

of them, whether obtained directly from coal tar or prepared from others so obtained, are known collectively as the coal-tar compounds. It is possible here to mention only a very few of the most important of the coal-tar compounds. These are as follows:

1. **Benzene** ( $C_6H_6$ ). This hydrocarbon is a colorless liquid boiling at  $79.6^\circ$ , and is a good solvent for most organic compounds, so that it is very useful in the laboratory. Both the liquid and its vapor are highly inflammable. One gram-molecule of the liquid on combustion evolves 749,200 cal. if the water formed is kept in a state of vapor. Benzene is used to a limited extent in place of gasoline in gasoline engines. It differs from the other hydrocarbons studied in that it reacts readily with nitric acid. The product of the reaction is *nitrobenzene* ( $C_6H_5NO_2$ ), a slightly yellowish liquid often called oil of mirbane:



When nitrobenzene is reduced with hydrogen, a colorless liquid known as *aniline* is formed. This has the formula  $C_6H_5NH_2$  and is the compound from which many of the *aniline dyes* are prepared.

2. **Toluene** ( $C_7H_8$ ). This is a liquid boiling at  $110^\circ$  and resembles benzene in its general properties. When oxidized, it forms *benzoic acid* ( $H \cdot C_7H_5O_2$ ), the sodium salt of which (sodium benzoate) is a common food preservative. When treated with nitric acid toluene forms *trinitrotoluene*  $C_7H_5(NO_2)_3$ . This is a white crystalline solid commonly known as T. N. T. It constituted the principal explosive used in the World War. From toluene there is also prepared the white solid known as *saccharine*, which is about 500 times as sweet as sugar. This was formerly used in foods as a sweetening agent, but in 1912 the government forbade its further use for that purpose.

3. **Naphthalene** ( $C_{10}H_8$ ). Ordinary moth balls are nearly pure naphthalene. The hydrocarbon is also used in making the well-known dye *indigo*. Formerly this dye was obtained from the indigo plant, which was cultivated in India, and a limited amount is still obtained from this source. Most of our supply, however, is prepared either from naphthalene or benzene.

4. **Anthracene** ( $C_{14}H_{10}$ ). This hydrocarbon is a nearly white solid and is used in the manufacture of *alizarin*, an important dye formerly obtained from the root of the madder plant, which was grown in France on a large scale for this purpose.

5. *Phenol (carbolic acid) ( $C_6H_5OH$ )*. This is a white crystalline solid, very caustic and poisonous. It is the source material for the preparation of *salicylic acid*. It is also used in the manufacture of *bakelite* and *condensite*. These are commercial products used in making such articles as buttons, umbrella handles, pipestems, and insulators in electrical apparatus. When treated with nitric acid phenol forms *picric acid* ( $C_6H_2(NO_2)_3OH$ ), a yellow solid which was used extensively as an explosive in the World War.

6. *Cresol (cresylic acid) ( $C_7H_7OH$ )*. There are three isomeric cresols. A mixture of these is obtained directly from coal tar and constitutes the basis of most of the disinfectants now on the market.

**Coal-tar dyes.** All dyes derived from coal tar are known as *coal-tar dyes* or *aniline dyes*. Many hundreds of these dyes have been prepared, of every imaginable color. Two of the most common of these, namely, *indigo* and *alizarin*, were formerly obtained from vegetable sources. Later, chemists found out how to make them in the laboratory, and now they are made in this way at a lower cost than they can be obtained from natural sources. The method of dyeing will be discussed in a later chapter.

Previous to the World War nearly all our dyes came from Germany. During the war this supply was cut off, and there was a temporary shortage of dyes. American chemists soon solved the problem connected with their production, and now the United States produces an adequate supply of dyes of the very highest grade.

**Historical.** The first aniline dye was made in 1856 by an English boy seventeen years of age. His name was William Perkin. The boy was assisting in the laboratory of an English University, and during the holidays he spent his time in trying to make *quinine*. In the course of some experiments with aniline he noticed that a colored substance of great beauty was produced. At this time all the dyes used were obtained from vegetable sources. Perkin got the idea that perhaps this new compound which he had prepared from aniline might be used as a dye. He finally

# SOME COAL PRODUCTS

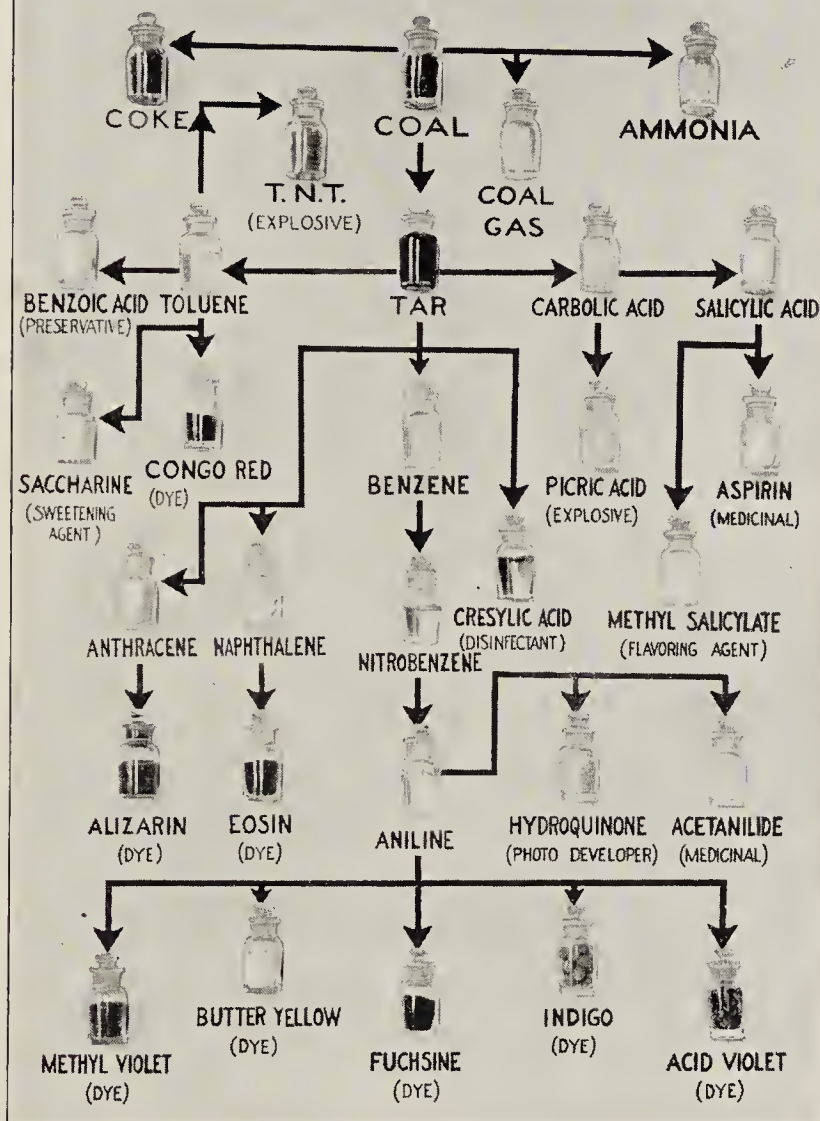


FIG. 172. Chart showing the source of a few important coal-tar compounds



succeeded in showing that it could be used and that it was superior to vegetable dyes in coloring power. This discovery led to others, and the investigation still continues, as shown by the fact that our dye plants employ hundreds of chemists. It is interesting to note that in 1906, fifty years after Perkin's discovery, he came to the United States and attended a great meeting held in New York City in honor of the fiftieth anniversary of the discovery of the first aniline dye.

The chart (Fig. 172) gives us some idea of the kind of compounds that are derived from coal tar and also the relation of the compounds to each other. Thus, *toluene* is obtained directly from coal tar, as indicated by the arrow, while from toluene (following the arrows) we obtain benzoic acid, trinitrotoluene (T. N. T.), saccharine, and Congo red. By simply following the arrows backward we can trace the *ancestry* of each compound named. Thus, the dyes at the bottom of the chart are all derived from aniline, but aniline is prepared from nitrobenzene and this from benzene, which is obtained directly from coal tar.

### EXERCISES

1. What is the meaning of the term *carbohydrate*? (See dictionary.)
2. Why does heating stop fermentation?
3. It is often said that milk sours readily during thunder showers. What should you say as to the truth of this statement?
4. Why do we use molasses rather than dextrose in making alcohol?
5. How could you tell the difference between methyl alcohol and ethyl alcohol?
6. By reference to Fig. 172 trace the steps in the formation of the following compounds from coal tar: (a) aspirin, (b) acetanilide, (c) saccharine, (d) indigo.
7. Why is sugar (or molasses) added in making bread?
8. Alcohol and gasoline boil at about the same temperature, and both are combustible. Why not use alcohol as a fuel in place of gasoline?
9. Can you suggest a method for obtaining ethyl alcohol from wood?
10. What weight of starch is necessary in making 100 kg. of pure dextrose?
11. 1 kg. of sucrose would yield what weight of invert sugar?

12. What weight of dextrose is necessary for the preparation of 10 kg. of the ordinary alcohol of the druggist, on the supposition that 95 per cent of the sugar undergoes fermentation?

13. What weight of benzene is necessary for the preparation of 100 kg. of aniline?

14. What volume of carbon dioxide is evolved in the fermentation of 100 g. of dextrose?

15. What weight of methyl alcohol would be required for the preparation of 50 kg. of formaldehyde?

16. Calculate the weight of lactic acid formed in the souring of 10 kg. of milk.

## CHAPTER XXX

### ORGANIC ACIDS: FATS AND OILS

**Organic acids.** Among the various compounds of carbon are included a number of acids which occur as constituents of certain forms of animal and vegetable life or the products derived from these organisms. Thus, *citric acid* is present in lemons and grapefruit, *lactic acid* in sour milk, and *acetic acid* in vinegar. These acids are known collectively as the *organic acids*. They occur either in the form of the free acid or of some derivative of the acid. The most common of these acids contain the elements hydrogen, carbon, and oxygen. Like the hydrocarbons, they can be arranged in series, one of the most important of which is known as the *fatty acid series*.

**The fatty acid series.** A few of the most important members of this series are given in the following table. They are all monobasic, — a fact indicated in the formula by separating the replaceable hydrogen atom from the rest of the molecule.

#### SOME FATTY ACIDS

$\text{H} \cdot \text{CHO}_2$	. . . . .	formic acid, a liquid boiling at 100.5°
$\text{H} \cdot \text{C}_2\text{H}_3\text{O}_2$	. . . . .	acetic acid, a liquid boiling at 118.1°
$\text{H} \cdot \text{C}_4\text{H}_7\text{O}_2$	. . . . .	butyric acid, a liquid boiling at 163.5°
$\text{H} \cdot \text{C}_{16}\text{H}_{31}\text{O}_2$	. . . . .	palmitic acid, a solid melting at 64°
$\text{H} \cdot \text{C}_{18}\text{H}_{35}\text{O}_2$	. . . . .	stearic acid, a solid melting at 69.3°
$\text{H} \cdot \text{C}_n\text{H}_{2n-1}\text{O}_2$	. . . . .	general formula, $n$ being the number of carbon atoms

Of these, acetic acid deserves special mention.

**Acetic acid ( $\text{H} \cdot \text{C}_2\text{H}_3\text{O}_2$ ).** This is the acid which gives the sour taste to vinegar. It is prepared commercially by the distillation of wood (p. 136). It is a colorless liquid and has a





are brought into intimate contact, and the oxidation takes place rapidly as the liquid trickles down over the shavings. The resulting vinegar is drawn off at the bottom (*B*) of the cask.

Instead of starting with cider, one may use almost any substance which contains starch or sugar, these compounds first being changed into alcohol, as explained in the manufacture of alcohol. In this way *malt vinegar* is prepared from starch and *sugar vinegar* from sugar residues. The cheapest vinegar is made from pure dilute alcohol and is known as *distilled vinegar*. It is colorless and leaves almost no residue upon evaporation.

A Federal law requires that all vinegar shall contain not less than 4 per cent acetic acid. In addition to the acid, vinegar prepared from fruits and grains contains certain solids derived from the source materials. It is by studying the character of these solids left upon evaporating a sample of vinegar that the chemist is able to determine the source of the vinegar.

**Acids belonging to other series.** In addition to the fatty acids the following organic acids deserve special mention:

**Lactic acid ( $\text{H} \cdot \text{C}_3\text{H}_5\text{O}_3$ ).** Reference has already been made to this acid (p. 395). It is a sirupy liquid and is formed when milk sours.

**Tartaric acid ( $\text{H}_2 \cdot \text{C}_4\text{H}_4\text{O}_6$ ).** This is a white solid and occurs in many fruits, either in the free state or in the form of its salts. The acid potassium salt  $\text{KHC}_4\text{H}_4\text{O}_6$  occurs in the juice of grapes. When the juice ferments in the manufacture of wine, this salt, being insoluble in alcohol, is deposited on the sides of the cask, and in this impure form it is known as *argol*. When purified it forms a white solid, which is sold under the name of *cream of tartar* and is used in baking powders. The acid itself is often used in soft drinks.

**Citric acid ( $\text{H}_3 \cdot \text{C}_6\text{H}_5\text{O}_7$ ).** This acid occurs in citrus fruits, such as lemons and grapefruit. It is a white solid, soluble in water.

**Oleic acid ( $\text{H} \cdot \text{C}_{18}\text{H}_{33}\text{O}_2$ ).** The derivatives of this acid constitute the principal part of many oils and liquid fats. The acid itself is an oily liquid.

**Oils and fats derived from animal and vegetable sources.**

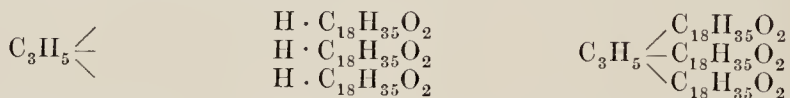
In the discussion of petroleum it was pointed out that the various oils derived from petroleum are known as *mineral oils*, since, like the minerals, they are obtained from the earth. There are a great many other oils and fats, such as olive oil, lard, and butter, that are derived from vegetable and animal sources. These two classes of oils, namely, (1) the mineral oils and (2) those derived from vegetable and animal sources, are entirely different in composition and chemical conduct. The mineral oils are hydrocarbons; the animal and vegetable oils, on the other hand, are composed almost wholly of mixtures of three compounds known as *olein*, *palmitin*, and *stearin*. Olein is a thick, colorless liquid and is the principal constituent of the oils such as olive oil and cottonseed oil. Palmitin and stearin are white solids and constitute the greater part of solid fats, such as tallow. In addition to these three constituents the vegetable and animal oils contain small percentages of other compounds, derived from the source material, and it is these compounds that give to each oil and fat its individual characteristics.

**Composition of olein, palmitin, and stearin.** We learned early in our study of chemistry that the molecules of all acids contain one or more hydrogen atoms which can be replaced by metals, and that the resulting compounds are called *salts*. Similarly, these same hydrogen atoms can be replaced by hydrocarbon radicals, and the resulting compounds are called *etheral salts* or, more often, *esters*. Now olein, palmitin, and stearin are esters formed by displacing the hydrogen atoms in oleic, palmitic, and stearic acids respectively by the hydrocarbon radical  $C_3H_5$ . This radical is tervalent and is known as glyceryl, since it is present in ordinary glycerin,  $C_3H_5(OH)_3$ , or, as often written,  $C_3H_5 \begin{smallmatrix} \diagup OH \\ | OH \\ \diagdown OH \end{smallmatrix}$ . Since the glyceryl radical is tervalent, and therefore replaces three atoms of hydrogen, and since oleic, palmitic, and stearic acids each contain but one

replaceable hydrogen atom in the molecule, it is evident that three molecules of each acid must enter into the formation of each molecule of the ester derived from the acid. The relation in composition between these acids and the corresponding esters is shown in the following formulas:



The composition of these esters may be more readily grasped by using structural formulas. Selecting stearin as an example, the relation between the glyceryl radical, stearic acid, and stearin may be represented as follows:



The tervalent glyceryl radical (exists only in combination with other elements or radicals)

Three molecules of stearic acid, each containing one replaceable hydrogen atom

Stearin, derived from the three molecules of stearic acid by displacing the three atoms of hydrogen by the tervalent glyceryl radical

**Butter fat and oleomargarine.** While butter fat, like other fats, consists principally of olein, palmitin, and stearin, its characteristic flavor is due to the presence of small quantities of other fats present in milk. Oleomargarine differs from butter mainly in the fact that a smaller percentage of the fats characteristic of butter is present. It is made from the fats obtained from cattle and hogs. Sometimes vegetable oils, such as coconut oil and cottonseed oil, are used. These fats are churned with milk or mixed with a small quantity of butter, in order to furnish the necessary fat to give the butter flavor.

In appearance oleomargarine differs from most butter in being nearly colorless. While it is a common practice to color butter artificially, the Federal law permits the coloring of oleomargarine only upon the payment of a tax of 10 cents for each pound colored. Many of the states, however, have laws forbidding the sale of oleomargarine that is artificially colored, even though the Federal tax has been paid.

**The hydrogenation of fats ; changing oils into solid fats.** It will be noted that stearin differs from olein in composition in that it contains six more atoms of hydrogen in each molecule. Now, if hydrogen is brought in contact with olein under proper conditions and in the presence of a suitable catalytic agent (finely divided nickel is used), the olein takes up the additional hydrogen and is changed into the solid stearin. This process is called the hydrogenation of fats. It is possible in this way to change the oils into solid fats which are adapted for use as foods and as a material for making soaps.

**The proteins.** The term *protein* is applied to a large class of complex nitrogenous compounds which are everywhere abundant in animal and vegetable organisms and which constitute the principal part of the tissues of the living cell. The casein of milk, gluten of flour, and albumen of egg will serve as examples of protein matter. The proteins all contain nitrogen, carbon, hydrogen, and oxygen, and some contain sulfur and phosphorus in addition.

## FOODS

**Composition and function of foods.** While the compounds present in our foods are very numerous and often exceedingly complex, yet they may all be included under a few general heads ; namely, *proteins, fats, carbohydrates, mineral matter, and water*. Since the mineral matter is left as a residue when the food is burned, it is listed as *ash* in reporting the analysis of foods. In addition to the above constituents many foods contain small percentages of substances known as *vitamins*, which are essential to life. The composition of a few of the more common foods is given in the table on the following page, taken from Sherman's "Chemistry of Food and Nutrition."

In general it may be stated that the proteid matter in our food serves to replace the worn-out tissues of our bodies, as well as to supply material for growth. The carbohydrates and fats are more or less interchangeable, since both are oxidized



in the body and serve as a source of heat and muscular energy. The mineral matter supplies the material for building up the solid tissues of the body and has, in addition, other more complex functions. The proteid matter may fulfill the same function as the fats and carbohydrates if the latter are lacking in our foods. Since the various constituents of our foods serve different purposes, it is evident that a proper mixture of these constituents is essential to the health of the individual.

	WATER (Per cent)	PROTEIN (Per cent)	FAT (Per cent)	CARBO- HYDRATES (Per cent)	ASH (Per cent)
Beef free from visible fat . . . . .	73.8	22.1	2.9		1.2
Ham, smoked, lean . . . . .	53.5	20.2	20.8		5.5
Salmon . . . . .	64.6	21.2	12.8		1.4
Eggs . . . . .	73.7	14.8	10.5		1.0
Milk . . . . .	87.0	3.3	4.0	5.0	0.7
Butter . . . . .	11.0	1.0	85.0		3.0
Oatmeal . . . . .	7.3	16.1	7.2	67.5	1.9
Rice . . . . .	12.3	8.0	0.3	79.0	0.4
Wheat flour . . . . .	11.9	13.3	1.5	72.7	0.6
Bread, white . . . . .	35.3	9.2	1.3	53.1	1.1
Beans, dried . . . . .	12.6	22.5	1.8	59.6	3.5
Corn, green . . . . .	75.4	3.1	1.1	19.7	0.7
Potatoes . . . . .	78.3	2.2	0.1	18.4	1.0
Tomatoes . . . . .	94.3	0.9	0.4	3.9	0.5
Apples . . . . .	84.6	0.4	0.5	14.2	0.3

**Vitamins.** Experiments in recent years have shown that in order that the body may grow and maintain its health there must be present in our foods, in addition to protein, fats, carbohydrates, and mineral matter, small quantities of certain substances which are known as *vitamins*. Only one of these has been obtained in a crystalline state and little is known of them beyond their physiological effects. Foods from which they have been extracted, although containing the necessary quantities of protein, carbohydrates, and fats, no longer nourish the body and maintain health.

**Varieties of vitamins.** At least five kinds of vitamins are known to exist. The names of these, together with the function of each and some food which is particularly rich in each, are as follows:

1. **Fat-soluble A.** Promotes growth, keeps the body in good condition, and thus prevents disease in general. Present in milk and butter.

2. **Water-soluble B.** Prevents the disease known as beri-beri. Present in fresh vegetables and yeast.

3. **Water-soluble C.** Prevents scurvy. Present in the juices of the tomato, the orange, and the lemon.

4. **Fat-soluble D.** Prevents the disease known as rickets. Present in cod-liver oil and green vegetables.

5. **Fat-soluble E.** Necessary for reproduction and growth of young. Present in wheat germs.

All five kinds are abundant in green vegetables such as lettuce and spinach, and in milk. Just how these vitamins act to promote growth and prevent disease is not known.

**Diet requirements.** In selecting our foods, then, it is essential not only that we secure the right proportion of protein, fats, carbohydrates, and mineral matter, but we must also consider whether the foods selected contain these ingredients in a palatable and digestible condition. Especially must we make such a selection as will furnish us with the necessary vitamins; in other words, *we must take into consideration quality as well as quantity of food*. For these reasons some foods, such as milk, may not seem to rank high as an economical food considered simply from its content of fat, carbohydrate, and protein; yet when we take into account the character of the constituents in milk, and especially its vitamin and mineral content, its effect in maintaining health makes it one of our most valuable foods.

**Fermentation.** We have already met with the following kind of fermentation:

1. *Alcoholic fermentation* (p. 403), which consists in the decomposition of a sugar into alcohol and carbon dioxide.

2. *Lactic fermentation* (p. 395), in which lactose (milk sugar) is decomposed into lactic acid.

3. *Acetic fermentation* (p. 413), in which alcohol is oxidized to acetic acid and which serves for the manufacture of vinegar.

Many other kinds of fermentation are known, but their study is beyond the scope of this book. The changes which take place are all produced through the growth of some micro-organism in the solution of the compound undergoing fermentation, each kind of fermentation being produced by some special organism. The microorganism acts by secreting a product known as an *enzyme*, and it is really the enzyme which brings about the change. Strictly speaking, therefore, the microorganisms do not directly cause fermentation. Their function is that of a factory for producing enzymes, and it is the enzymes that cause the changes known as fermentation.

Since various substances undergo fermentation on exposure to air, as in the change of cider into vinegar, it is evident that the seeds or spores of the plants causing fermentation must exist in the air and thus find their way into the solutions.

#### EXERCISES

1. For what purpose have we used formic acid? Consult the dictionary for the derivation and significance of the word *formic*.
2. What weight of dextrose would be required to prepare 100 kg. of vinegar containing the legal quantity of acetic acid, on the supposition that all the sugar is converted into acetic acid?
3. Account for the fact that potassium-acid tartrate separates when grape juice ferments.
4. Aluminum is a trivalent metal. Write the formula for aluminum stearate; aluminum tartrate; aluminum citrate.
5. Derive the formula for the ester formed by displacing the hydrogen of butyric acid by the glyceryl radical.
6. The Pure Food and Drugs Act requires that all vinegars must contain not less than 4 g. of acetic acid in 100 g. of vinegar. Calculate approximately the percentage of sugar that must be present in cider in order that the vinegar formed from it may fulfill the requirement of the law as to the acetic-acid content.

## CHAPTER XXXI

### THE METALS

**The metals.** The elements so far considered have nearly all been those whose compounds with oxygen and hydrogen are *acids*, and they are called the *acid-forming* elements or the nonmetals. Those which we shall now study are known collectively as the *metals*. The hydroxides of the metals are *bases*, and on this account the *metals are sometimes defined as those elements whose hydroxides are bases*. When the hydroxide of a metal or any of the simple salts derived from the hydroxide are dissolved in water, the metallic element forms the cation and carries a positive charge.

The distinction between a metal and a nonmetal is not a very sharp one, since the hydroxides of a number of elements act as bases under some conditions and as acids under others. We have seen that antimony is an element of this kind.

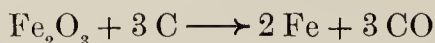
**Properties of the metals.** The general properties of the metals are as follows: (1) They are all solids with the exception of mercury, which is a liquid. (2) Most of them have a high density, although three of them, namely, lithium, sodium, and potassium, are lighter than water. (3) They are good conductors of heat and electricity. (4) With the exception of gold and copper they have a silvery luster. (5) As a rule they are *malleable*, or capable of being hammered out into thin foil, and they can also be drawn out into the form of wire; this property is designated as *ductility*. (6) Most of them combine readily with oxygen and sulfur, and their surfaces quickly tarnish on exposure to air. A few of them, such as gold and platinum, have little chemical activity, and this property makes them especially valuable.



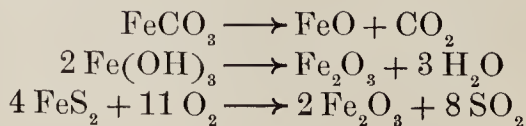
**Occurrence of metals in nature.** A few of the metals are found in nature in the free state. Among these are gold, platinum, and frequently copper. They are usually found combined with other elements in the form of oxides or salts of various acids. Silicates, carbonates, sulfides, and sulfates are the most abundant of these salts. *All inorganic substances occurring in nature, whether they contain a metal or not, are called minerals. Those minerals from which a useful substance can be extracted are called ores of the substance.*

**Extraction of metals: metallurgy.** The process of extracting a metal from its ores is called the *metallurgy* of the metal. The metallurgy of each metal presents peculiarities of its own, but there are several methods of general application which are very frequently employed.

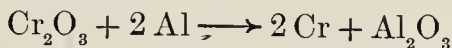
1. **Reduction of an oxide with carbon.** Many of the metals occur in nature in the form of oxides. When some of these oxides are heated to a high temperature with carbon, the oxygen combines with the carbon and the metal is set free. Iron, for example, occurs largely in the form of the oxide  $\text{Fe}_2\text{O}_3$ . When this is heated with carbon the reaction expressed in the following equation takes place:



Many ores other than oxides may be changed into oxides, which can then be reduced by carbon. The conversion of such ores into oxides is ordinarily accomplished by heating, and the process is called *roasting*. Many carbonates and hydroxides decompose directly into the oxide on being heated. Sulfides, on the other hand, must be heated in a current of air, the oxygen of the air entering into the reaction. The following equations will serve to illustrate these changes in the case of the ores of iron:



2. *Reduction of an oxide with aluminum.* Not all oxides, however, can be reduced by carbon. In such cases aluminum may be used. Thus, chromium may be obtained in accordance with the following equation:



This method was first used by the German chemist Goldschmidt and is called the *Goldschmidt method*.

3. *Electrolysis.* In recent years increasing use is being made of the electric current in the preparation of metals. In some



FIG. 174. View of a group of power plants at Niagara Falls

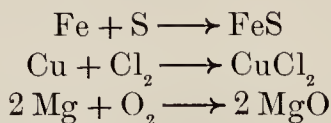
cases the separation of the metal from its compounds is accomplished by passing the current through a solution of a suitable salt of the metal, the metal usually being deposited upon the cathode. This method, however, is not applicable in the case of metals that are readily acted upon by water; in such cases the current is passed through a fused compound of the metal, the chloride and hydroxide being best adapted to this purpose.

**Electrochemical industries.** Most of the electrochemical industries of the country are carried on where water power is abundant, since this furnishes the cheapest means for the generation of electrical energy. Niagara Falls is the most

important locality in this country for such industries, and many different electrochemical products are manufactured there (Fig. 174). Some industries depend upon electrolytic processes, while in others the electrical energy is used merely as a source of heat. In the latter case the process is called *thermoelectric*.

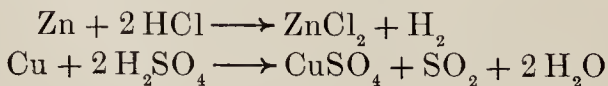
**Preparation of compounds of the metals.** Since the compounds of the metals are so numerous and so varied in character, there are many ways of preparing them. In many cases the properties of the substance to be prepared, or the material available for its preparation, suggest a rather unusual way. There are, however, a number of general principles which are constantly applied in the preparation of the compounds of the metals, and a clear understanding of them will save much time and effort in remembering the details in any given case. Some of the general methods for the preparation of compounds are the following:

1. *By direct union of two elements.* This is usually accomplished by heating the two elements together. Thus, the sulfides, chlorides, and oxides of a metal can usually be obtained in this way. The following equations serve as examples of this method:



2. *Treatment of a metal, or its oxide or hydroxide, with an acid.*

Since most of the metals are produced commercially in a high degree of purity, the metals themselves are often the most convenient starting point for the preparation of their compounds on a small scale in the laboratory. For example, the salts of zinc and copper are frequently made in this way:



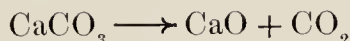
In the industries the hydroxide or oxide is more likely to be employed, since it is usually found in nature or is of easy preparation. For example, soluble calcium salts are often prepared from lime ( $\text{CaO}$ ), as in the case of the nitrate:



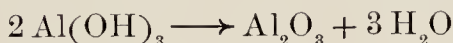
3. *By the decomposition of a compound.* This decomposition may be brought about either by heat alone or by the combined action of heat and a reducing agent. Thus, when the nitrate of a metal is heated, the oxide of the metal is usually obtained. Copper nitrate, for example, decomposes as follows:



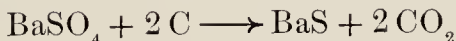
Similarly, the carbonates of the metals yield oxides, thus:



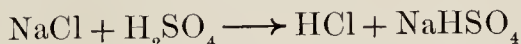
Most of the hydroxides form an oxide and water when heated:



When heated with carbon, sulfates are reduced to sulfides, thus:



4. *Displacement of a volatile acid.* When a nonvolatile acid acts upon a salt of a volatile acid, the latter is displaced in accordance with the general principles of equilibrium, *provided the volatile acid is sparingly soluble* in any liquid which may be present. For example, the reaction of sulfuric acid with sodium chloride goes on to conclusion if the sulfuric acid employed is quite concentrated, for hydrogen chloride is very sparingly soluble in this liquid:



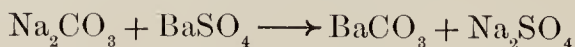
In dilute solution the reaction results in an equilibrium, for in this case the hydrogen chloride is freely soluble in the solution.

5. *Methods based on equilibrium in solution.* In the preparation of compounds the first requisite is that the reactions



chosen shall be of such a kind as will go on to completion. In the chapter on chemical equilibrium (p. 243) it was shown that reactions in solution may become complete in either of three ways: (1) a gas may be formed which escapes from solution; (2) an insoluble solid may be formed which precipitates; (3) two different ions may combine to form undissociated molecules. By the judicious selection of materials these principles may be applied to the preparation of a great variety of compounds, and illustrations of such methods will very frequently be found in the subsequent pages.

6. *By fusion methods.* It sometimes happens that substances which are insoluble in water and in acids, and which cannot therefore be brought into double decomposition in the usual way, are soluble in other liquids, and when dissolved in them can be decomposed and converted into other desired compounds. Thus, barium sulfate is not soluble in water, and since sulfuric acid is less volatile than most other acids, it cannot easily be driven out from this salt. When brought into contact with melted sodium carbonate, however, it dissolves in it, and since barium carbonate is insoluble in melted sodium carbonate, double decomposition takes place:



When the cooled mixture is dissolved in water, the sodium sulfate formed in the reaction, together with any excess of sodium carbonate which may be present, dissolves. The barium carbonate can then be filtered off and converted into any desired salt by the processes already described.

**Important insoluble compounds.** Since precipitates play so important a part in the reactions which substances undergo, as well as in the preparation of many chemical compounds, it is important to know what substances are insoluble in water. Knowing this, we can in many cases predict reactions under certain conditions, and are assisted in devising ways to prepare desired compounds. While there is no general rule which will

enable one to foretell the solubility of any given compound, nevertheless the following general statements can be made which will be of great assistance. There are some exceptions to these statements, but they are of little practical importance.

1. **Hydroxides.** All hydroxides are insoluble in water save those of ammonium, sodium, potassium, calcium, barium, and strontium.

2. **Nitrates.** All nitrates are soluble in water.

3. **Chlorides.** All chlorides are soluble in water save silver and mercurous chlorides. (Lead chloride is but slightly soluble.)

4. **Sulfates.** All sulfates are soluble in water save those of barium, strontium, and lead. (Sulfates of silver and calcium are only moderately soluble.)

5. **Sulfides.** All sulfides are insoluble in water save those of ammonium, sodium, and potassium. The sulfides of calcium, barium, strontium, and magnesium are insoluble in water, but are changed by hydrolysis into acid sulfides which are soluble; on this account they cannot be prepared by precipitation.

6. **Carbonates, phosphates, and silicates.** All normal carbonates, phosphates, and silicates are insoluble in water save those of ammonium, sodium, and potassium.

### EXERCISES

1. What is the position, in the electrochemical series, of those metals found in a free state in nature?

2. Mention an important compound, already studied, that is prepared by an electrolytic process; also one in which electrical energy is used merely as a source of heat.

3. In general which compounds of a metal serve best for the preparation of the other compounds of the metal?

4. Write equations representing four different ways of preparing  $\text{Cu}(\text{NO}_3)_2$ .

5. Give one or more methods for preparing each of the following compounds:  $\text{CaCl}_2$ ,  $\text{PbCl}_2$ ,  $\text{BaSO}_4$ ,  $\text{CaCO}_3$ ,  $(\text{NH}_4)_2\text{S}$ ,  $\text{Ag}_2\text{S}$ ,  $\text{PbO}$ ,  $\text{Cu}(\text{OH})_2$  (for solubilities, see last paragraph of chapter). State in each case the general principle involved in the method of preparation chosen.

## CHAPTER XXXII

### THE ALKALI METALS

METAL	ATOMIC WEIGHT	DENSITY	MELTING POINT	BOILING POINT	FIRST PREPARED
Lithium (Li) . . .	6.940	0.53	186.0°	1200°(?)	Arfvedson, 1817
Sodium (Na) . . .	22.997	0.97	97.5°	880°	Davy, 1807
Potassium (K) . . .	39.10	0.86	62.3°	760°	Davy, 1807
Rubidium (Rb) . .	85.44	1.53	38.5°	700°	Bunsen, 1861
Cesium (Cs) . . .	132.81	1.90	26.0°	670°	Bunsen, 1860

**Characteristics of the family.** The elements listed in the above table constitute a family in Group I of the periodic table. They are called the *alkali metals* for the reason that the most familiar members of the family, namely, sodium and potassium, are constituents of compounds that have long been known as alkalies.

**Historical.** Previous to the discovery of sodium and potassium in 1807, the hydroxides of these metals were thought to be elementary in character. After it had been discovered that water could be decomposed by the electric current, the English chemist Humphry Davy (Fig. 76) tried the effect of the electric current upon a piece of solid potassium hydroxide, thinking that it might be possible to decompose this substance just as water had been decomposed. In announcing the results of his experiment Davy states that "small globules having a high metallic luster and being precisely similar in visible character to quicksilver appeared, some of which burned with explosions and bright flames as soon as they were formed, and others remained and were merely tarnished and finally covered by a white film which formed on their surface." These globules consisted of the element potassium, which Davy had thus prepared for the first time. This memorable experiment

was performed on the sixth of October, 1807. A few days later Davy succeeded in isolating sodium in a similar way.

While Davy is generally regarded as the discoverer of sodium and potassium, it should be added that Edgar F. Smith (Fig. 27), in his book "Chemistry in America," points out that the American chemist James Woodhouse of Philadelphia prepared the element at about the same time that Davy obtained it. Since Woodhouse died in 1809, it is possible that his discovery may have antedated that of Davy.

The alkali metals, as shown in the above table, are light metals of low melting point. They are very soft and when pure have a bright metallic luster. Their position at the head of the electrochemical series designates them as very active metals; hence they do not occur free in nature. They are univalent, and, with very few exceptions, their compounds are white solids, soluble in water.

Sodium and potassium are by far the most important members of the family. Rubidium and cesium are very difficult to prepare. They form compounds analogous in formulas and general properties to those of sodium and potassium. Because of their high cost, neither the metals themselves nor their compounds are used to any extent.

## LITHIUM

**Occurrence and properties.** Lithium is distributed widely but in small quantities. It is found in certain mineral waters (lithia waters) and in nearly all igneous rocks. From these rocks it finds its way into the soil and is taken up by certain plants such as the sugar beet and tobacco. When these plants are burned, the lithium present is changed into lithium carbonate ( $\text{Li}_2\text{CO}_3$ ), which remains in the ashes.

Lithium is the lightest of all metals, being only about half as heavy as water. It is difficult to prepare and has no commercial use. Some of its compounds are used in medicine and in the manufacture of opal glass and enamels.

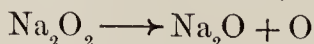


## THE COMPOUNDS OF SODIUM

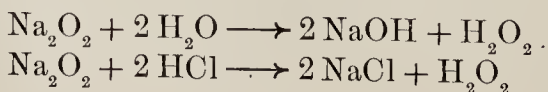
**NOTE.** The metal sodium, as well as its hydroxide, was considered in Chapter XVI. It is desirable for the student to review this chapter in connection with the study of the other members of the family.

**General.** In addition to sodium hydroxide (p. 193) sodium forms a large number of compounds. With the exception of the nitrate all these compounds are prepared from the chloride, since it is so abundant and inexpensive. The processes involved are often complicated, owing to the fact that the compounds of sodium are all soluble and therefore cannot be prepared directly from the chloride by precipitation; moreover, the chloride is a salt of a strong acid and is not readily acted upon by most other acids. Experiments have shown that the most economical method of procedure consists either in first changing the chloride into the hydroxide by the electrolysis of its aqueous solution or in converting it into the carbonate by the methods to be described. Since the hydroxide is a base and the carbonate is a salt of a very weak volatile acid, both are readily changed into other compounds.

**The oxides of sodium.** The metal forms two well-known oxides, namely, sodium oxide ( $\text{Na}_2\text{O}$ ) and sodium peroxide ( $\text{Na}_2\text{O}_2$ ). The former is obtained, mixed with peroxide, when sodium is burned in a limited supply of air. The peroxide is more easily obtained pure, and is of much the greater importance, since it serves as an excellent oxidizing agent. It is a yellowish-white powder prepared by passing air, freed from moisture and carbon dioxide, through an iron tube containing sodium heated to about  $300^\circ$ . While the pure compound is stable toward heat, in the presence of an oxidizable substance it gives up half of its oxygen:



It is readily acted upon by water and by acids:



The hydrogen peroxide formed in the reactions decomposes into water and oxygen unless the temperature is kept low. It will be recalled that the reaction with water serves as one of the methods given for preparing oxygen.

**Sodium chloride (common salt) ( $\text{NaCl}$ ).** Sodium chloride is very widely distributed in nature. Thick strata, evidently deposited by the evaporation of salt water, are found in many

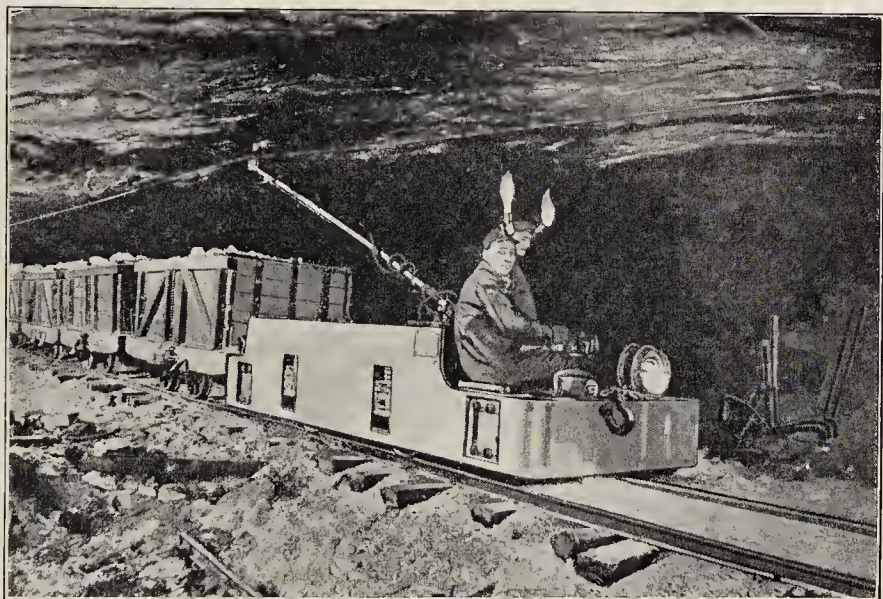


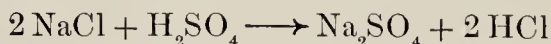
FIG. 175. View in the mines of the Retsof Salt Company, New York

places. In the United States the most important localities for salt are Michigan, New York, Ohio, and Kansas. Sometimes the salt is mined (Fig. 175), especially if it is in the pure form called *rock salt*. Very frequently a strong brine is pumped from deep wells sunk into the salt deposit and is then evaporated in large pans until the salt crystallizes out. The crystals are in the form of small cubes and are anhydrous but are apt to contain some water mechanically inclosed. Salt melts at  $801^{\circ}$  and just above this temperature has considerable vapor pressure.

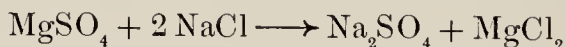
Salt is used in the preparation of nearly all substances containing either sodium or chlorine. These include many products of the highest importance to civilization, such as soap, glass, hydrochloric acid, soda, and bleaching powder. To meet these demands about 7,000,000 tons of salt are produced annually in the United States. Small quantities are essential to animal life. Pure salt does not absorb moisture, though we usually think it does; the fact that ordinary salt becomes moist in air is due to the presence of certain deliquescent compounds, especially the chlorides of calcium and magnesium.

**Sodium bromide (NaBr); sodium iodide (NaI).** These compounds resemble sodium chloride in their physical properties. They can be prepared by the action of bromine and iodine respectively upon a solution of sodium hydroxide (p. 312). They are used to a limited extent in photography and in medicines.

**Sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>).** This salt is prepared by the action of sulfuric acid upon sodium chloride, hydrogen chloride being formed at the same time (p. 184):

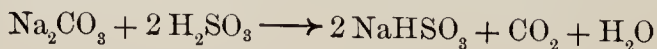


It is also prepared by the action of sodium chloride upon magnesium sulfate, the latter being obtained in large quantities in the manufacture of potassium chloride:

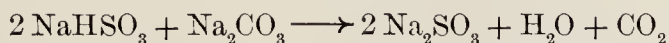


The anhydrous sodium sulfate is a white solid. It is readily soluble in water and, under ordinary conditions, crystallizes out as the hydrate, Na<sub>2</sub>SO<sub>4</sub> · 10 H<sub>2</sub>O (known as *Glauber's salt*). Large quantities of sodium sulfate are used in making sodium carbonate and glass. The salt is also used in medicine.

**Sulfites of sodium.** The acid sulfite, NaHSO<sub>3</sub>, often called sodium bisulfite, is formed by saturating a solution of sodium carbonate with sulfur dioxide. Sulfurous acid is first formed by the union of the dioxide with water, and this decomposes the carbonate:

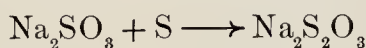


The normal sulfite,  $\text{Na}_2\text{SO}_3$ , is prepared by adding sodium carbonate to a saturated solution of the acid sulfite in the proportion indicated in the following equation:



Both of the sulfites of sodium readily absorb oxygen, forming the corresponding sulfates; they are therefore reducing agents. They are used to some extent as bleaching agents and as preservatives.

**Sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ).** This salt is made by boiling a solution of sodium sulfite with sulfur:

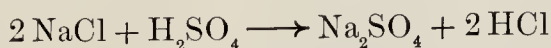


The hydrate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ , is frequently called *sodium hyposulfite*, or simply *hypo*. It is used in photography and in the bleaching industry to absorb the excess of chlorine which is left upon the bleached fabrics.

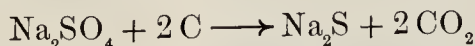
**Sodium carbonate (soda ash) ( $\text{Na}_2\text{CO}_3$ ).** There are two different processes now employed in the manufacture of this salt. These processes are known as the Leblanc process and the Solvay process, respectively, from the names of the chemists who devised them (Figs. 176, 177).

1. **Leblanc process.** This older process involves several distinct reactions, as shown in the following equations:

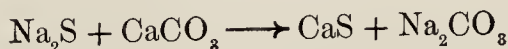
(a) Sodium chloride is first converted into sodium sulfate:



(b) The sodium sulfate is next reduced to sodium sulfide by heating it with carbon:



(c) The sodium sulfide is then heated with calcium carbonate, when the following reaction takes place:





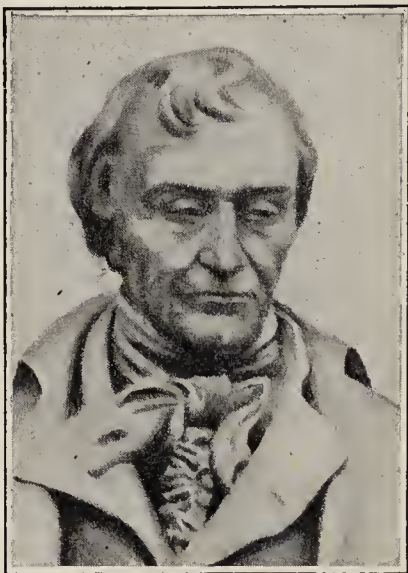


FIG. 176. Nicolas Leblanc  
(1742-1806)

The French chemist who devised the method for making sodium carbonate from common salt. Previous to his time the supply of sodium carbonate came entirely from the ash of seaweeds. Leblanc's method proved to be a much cheaper source of the compound. The method was long used in the United States and is still used in England. The portrait shown here is taken from a statue erected in Paris in honor of Leblanc

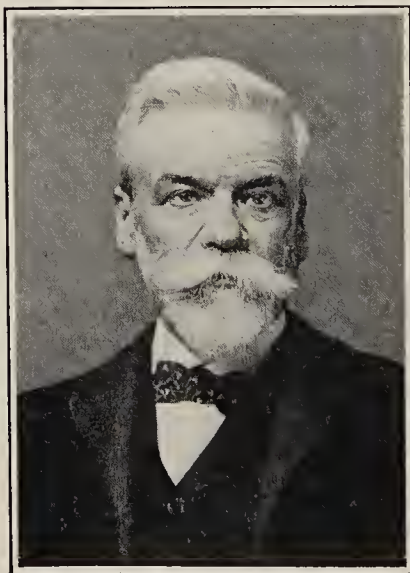


FIG. 177. Ernest Solvay  
(1835-1922)

A famous Belgian manufacturing chemist who developed the Solvay process for making sodium carbonate. This process has largely displaced the older one devised by Leblanc. The commercial success of this process brought Solvay great wealth, and he was very generous, distributing on his seventy-fifth birthday more than a million dollars for educational and philanthropic purposes

FIG. 178. Robert Wilhelm  
Bunsen (1811-1899)

A distinguished German chemist. Bunsen discovered rubidium and cesium by means of the spectroscope, an instrument devised by Bunsen and Kirchoff. He also devised a filter pump, a galvanic cell, a laboratory gas burner (Bunsen burner), and other useful apparatus. He worked out a method for preparing magnesium on a large scale and contributed much to our methods for analyzing gases

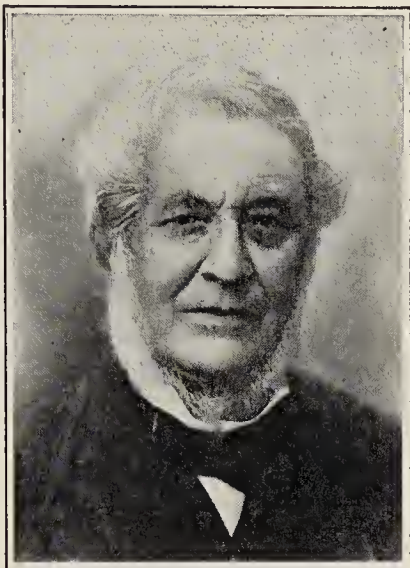
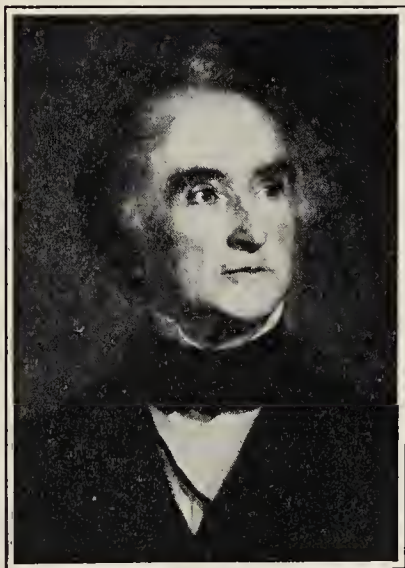
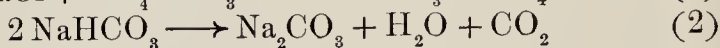


FIG. 179. Justus von Liebig  
(1803-1873)

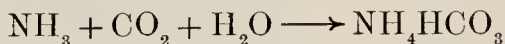
German chemist and teacher. He devised the method for analyzing organic compounds and was the first to prepare chloroform as well as a number of other useful compounds. He made important contributions in the applications of chemistry to agriculture. At the University of Giessen, Germany, he established a school of chemistry, the first in which the students used the laboratory method. Here many great chemists were trained



2. *Solvay process.* This more modern process depends upon reactions taking place *in solution* and represented in the equations



When concentrated solutions of sodium chloride and of ammonium hydrogen carbonate are brought together, the sparingly soluble sodium hydrogen carbonate is precipitated as represented in equation (1). This, when heated, is converted into the normal carbonate as indicated in equation (2). The ammonium chloride formed (equation (1)) is treated with lime (p. 219), ammonia being liberated. This ammonia, together with water and the carbon dioxide generated as indicated in equation (2), combine to form ammonium hydrogen carbonate:



This is treated with salt, and the process is begun over again according to equation (1).

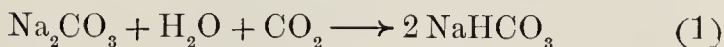
**Historical.** In former times sodium carbonate was made by burning seaweeds and extracting the carbonate from their ash. On this account the salt was called *soda ash*, and the name is still in common use. During the French Revolution this supply was cut off, and Napoleon offered a prize of 100,000 francs to anyone who would devise a way of making the carbonate directly from common salt. The prize was won by Leblanc (Fig. 176) in 1794, and the *Leblanc method* was used exclusively for many years. It is still used somewhat in England, but in the United States it has been entirely displaced by the *Solvay process*, which was devised by the Belgian chemist Solvay (Fig. 177) in 1863.

**By-products.** The substances obtained in a given process, aside from the main product, are called the *by-products*. The success of many processes depends upon the value of the by-products formed. Thus, hydrochloric acid, a by-product in the Leblanc process, is valuable enough to make the process pay, even though sodium carbonate can be made at lower cost in other ways.

**Properties of sodium carbonate.** Sodium carbonate combines with water to form a number of hydrates. The most common of these has the formula  $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$  and is known as *washing soda* or *sal soda*. The monohydrate  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  is also prepared and used commercially to some extent.

An aqueous solution of sodium carbonate has a mild alkaline reaction and is used for laundry purposes. Mere mention of the fact that the salt is used in the manufacture of glass, soap, and many chemical reagents will indicate its importance in the industries. It is one of the few soluble carbonates.

**Sodium hydrogen carbonate ( $\text{NaHCO}_3$ ).** This salt, called *bicarbonate of soda* or *baking soda*, is made by the Solvay process, as explained above, or by passing carbon dioxide into concentrated solutions of sodium carbonate:



It is an essential constituent of all baking powders.

**Commercial production of carbon dioxide.** Advantage is taken of the reaction expressed in equation (1) above for the purification of carbon dioxide on a large scale. Coal is burned under a steam boiler, and the resulting carbon dioxide is conducted into large towers filled with coke over which trickles a concentrated solution of sodium carbonate. The carbon dioxide is absorbed, forming sodium bicarbonate. The product is then heated by the steam generated in the boiler, forming carbon dioxide, which is collected, and sodium carbonate, which is used over again (equation (2), p. 434). The process thus becomes continuous.

**Sodium nitrate (Chile saltpeter) ( $\text{NaNO}_3$ ).** This substance is found in nature in certain arid regions where it has apparently been formed by the decay of organic substances in the presence of air and sodium salts. The largest deposits are in Chile, and most of the nitrate of commerce comes from that country. Fig. 180 shows a deposit of sodium nitrate in Chile after it has been broken apart by explosives. The commercial salt is prepared by dissolving the crude nitrate (known as *caliche*) in water, allowing the insoluble earthy materials to settle, and



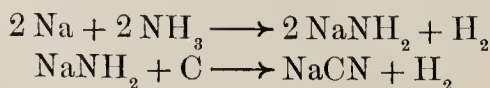
evaporating to crystallization the clear solution so obtained. Most of the soluble impurities remain in the mother liquors.

Since this salt is the only nitrate found extensively in nature, enormous quantities of it have been used in the preparation of nitric acid and of other nitrates and fertilizers. Large quantities are still used for these purposes, but it is gradually being displaced by nitrogen compounds prepared synthetically from the nitrogen of the air by methods already discussed (p. 220).



FIG. 180. Quarrying sodium nitrate in Chile

**Sodium cyanide (NaCN).** This salt of hydrocyanic acid (p. 254) readily dissolves gold and is used for extracting this metal when it is scattered in small quantities through earthy material. It can be prepared in a number of ways, but at present nearly all of our supply is obtained by heating a mixture of carbon and sodamide ( $\text{NaNH}_2$ ). The latter compound is a white solid prepared by the action of sodium on ammonia. The equations representing the preparation of sodamide and its conversion into sodium cyanide are as follows:



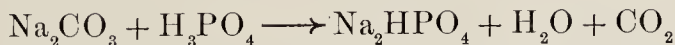
Sodium cyanide is a white solid. Its aqueous solution is strongly alkaline, owing to hydrolysis. The compound is not only extremely poisonous but in contact with acids evolves the very poisonous hydrogen cyanide (HCN) (p. 254).

**Bucher process for making sodium cyanide.** The American chemist Bucher has devised a process for making sodium cyanide by passing nitrogen through tubes containing a mixture of sodium carbonate, coke, and finely divided iron, the latter acting as a catalyzer. If the temperature is maintained at about  $1000^{\circ}$ , a reaction takes place resulting in the formation of sodium cyanide:



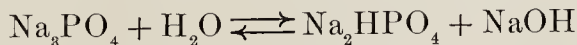
During the World War the government erected at Saltville, Virginia, a plant designed to produce by this process 10 tons of sodium cyanide daily. The plant was completed but was operated only on a limited scale when the armistice was signed. At its present stage of development the process can hardly compete with the sodium process for the manufacture of cyanides.

**The phosphates of sodium.** Sodium forms three salts with phosphoric acid, one normal and two acid salts. The most common of these is disodium phosphate ( $\text{Na}_2\text{HPO}_4$ ). It is prepared by the action of phosphoric acid upon sodium carbonate:



This salt crystallizes as the hydrate,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ .

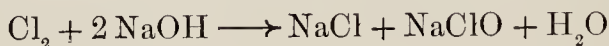
The normal phosphate,  $\text{Na}_3\text{PO}_4$ , dissolves readily in water, forming a strongly alkaline solution, owing to partial hydrolysis:



It is prepared by adding excess of sodium hydroxide to a solution of disodium phosphate and evaporating to crystallization. The sodium hydroxide reverses the reaction of hydrolysis as given above, and the normal phosphate separates as the hydrate,  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ . It is a common constituent of many of the

washing powders sold on the market. When added to water, it not only precipitates most of the mineral matter present, thus making the water soft, but at the same time it leaves the water slightly basic in reaction.

**Sodium hypochlorite ( $\text{NaClO}$ ).** This salt is prepared by the action of chlorine on a *cold* solution of sodium hydroxide :



Sodium hypochlorite is very unstable and can be obtained only in a dilute solution. This solution is a good oxidizing agent. It serves as an antiseptic in the treatment of wounds.

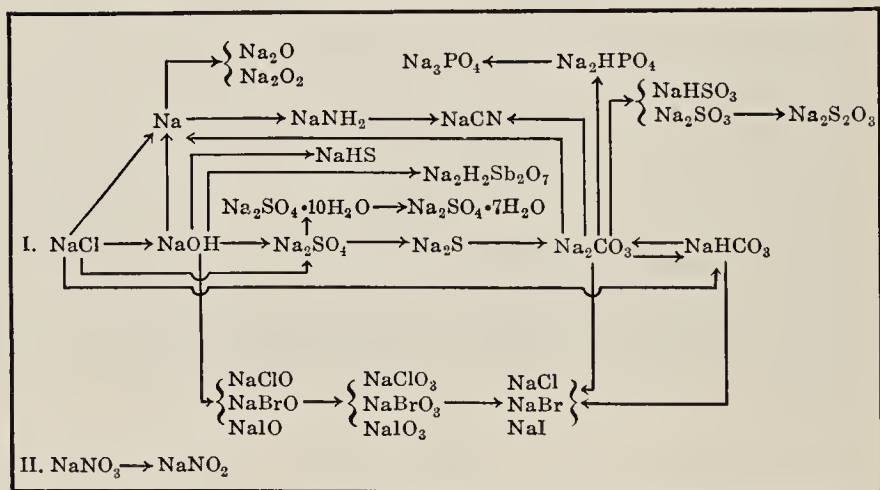


FIG. 181. Diagram showing steps in the preparation of important compounds of sodium, starting with sodium chloride or sodium nitrate

**Commercial preparation.** Sodium hypochlorite can be obtained commercially by electrolyzing a solution of sodium chloride under proper conditions. The electrolysis is carried out in such a way that the products formed, namely, chlorine and caustic soda, are not kept separate, as in the manufacture of these products (p. 178), but are liberated together, so that they react as fast as liberated in accordance with the above equation. It is also prepared from bleaching powder as follows: Water is added to the bleaching powder, whereby calcium hypochlorite ( $\text{Ca}(\text{ClO})_2$ ) is formed and

remains in solution. This is separated from the insoluble material, and a solution of sodium carbonate is added to the filtrate:



The calcium carbonate formed is insoluble and is filtered off, leaving the sodium hypochlorite in solution in the filtrate. When prepared in this way, the solution is known as *Javelle water*.

**Other compounds of sodium.** Sodium forms both the acid and normal salts of hydrosulfuric acid; namely,  $\text{NaHS}$  and  $\text{Na}_2\text{S}$ . The former is made by saturating a solution of sodium hydroxide with hydrogen sulfide and the latter by reducing sodium sulfate with carbon. *Sodium pyroantimonate* ( $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ ) is the least soluble of all the compounds of sodium. *Sodium chlorate* ( $\text{NaClO}_3$ ) is often used as an oxidizing agent as well as in the preparation of oxygen in the laboratory. *Sodium nitrite* ( $\text{NaNO}_2$ ) is of use in preparing many dyes.

## POTASSIUM

**Occurrence.** Potassium resembles sodium very closely in its properties. It is a rather abundant element, being a constituent of many igneous rocks, especially the feldspars and micas. Sea water, as well as most mineral waters, contains small percentages of its compounds. Very large deposits of the chloride and sulfate, associated with compounds of calcium and magnesium, occur in the region of Stassfurt, Germany, and are known as *Stassfurt salts*. Similar deposits consisting chiefly of the chloride (sylvite) occur in southern Alsace, France. It is also found in small quantities as the nitrate (saltpeter) and in many other forms.

The natural decomposition of rocks containing potassium gives rise to various compounds of the element in all fertile soils. It is absorbed by growing plants and is a necessary constituent of land plants, just as sodium is of sea plants. Some of the sea plants, however (for example, the giant algæ of the California coast), contain potassium chloride amounting in some cases to 30 per cent of their dry weight. In the land plants the potassium is present chiefly in the form of salts of



organic acids. When such plants are burned, the potassium remains in the ash as carbonate, and the crude carbonate so obtained was formerly the chief source of potassium compounds. In recent years, except during the period of the World War,

the Stassfurt deposits have constituted the chief source of these compounds.

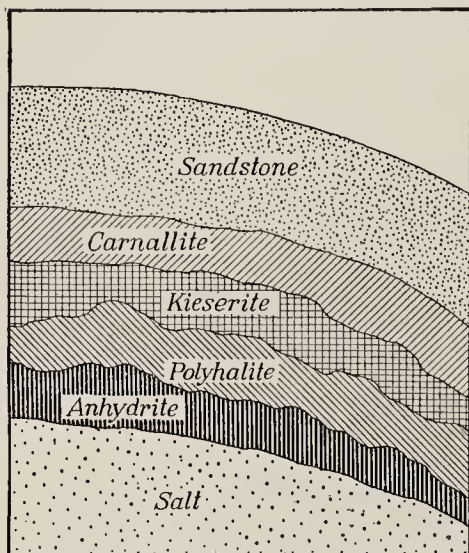


FIG. 182. Cross-section diagram of the Stassfurt salt deposits

**Stassfurt salts.** These salts, evidently deposited from sea water under peculiar geological conditions, form very extensive deposits in middle and north Germany, the most noted locality for working them being at Stassfurt. The deposits are very thick and rest upon an enormous layer of common salt. They are in the form of a series of strata, each consisting largely of a single mineral salt. Over thirty different

minerals are present, but some are in very small quantities. Fig. 182 shows a cross section of these deposits. While from a chemical standpoint these strata are salts, they are as solid and hard as many kinds of stone and are mined as stone or coal would be. Since the strata differ in general appearance, each can be mined separately, and the various minerals can be worked up by methods adapted to each particular case. The chief minerals of commercial importance in these deposits, together with the composition of each, are listed in the table below :

Sylvite . . . . .	KCl
Anhydrite . . . . .	$\text{CaSO}_4$
Carnallite . . . . .	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$
Kainite . . . . .	$\text{MgSO}_4 \cdot \text{KCl} \cdot 3 \text{H}_2\text{O}$
Kieserite . . . . .	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$
Schönite . . . . .	$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6 \text{H}_2\text{O}$

**Sources of potassium salts in the United States.** For a number of years previous to the World War almost the entire amount of potassium salts consumed in the United States was obtained from Germany. With the declaration of war this supply was cut off, and persistent efforts were made to develop an independent supply within our own borders sufficient to meet our needs, especially for making glass and fertilizers. As a result a limited amount was produced, and this production has continued. The sources of potassium salts in the United States are as follows:

1. *Natural brines.* The waters of certain partially dried-up lakes located in Nebraska and California yield on evaporation a mixture of salts containing varying amounts of potassium sulfate and potassium carbonate. Searles Lake in California is the most important of these and serves today as the greatest single source of potassium salts in the United States.

2. *Flue dust from blast furnaces and cement kilns.* This dust contains a small percentage of potassium salts. But little effort is made to recover these, so that a large amount of these salts goes to waste each year.

3. *Wastes in the production of alcohol from molasses.*

4. *Wastes in the beet-sugar industry.*

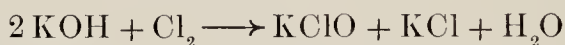
The United States imports yearly from Germany and France about 200,000 tons of potassium salts calculated as  $K_2O$ . The present production in the United States amounts to about 22,000 tons. Potassium salts have been found in boring gas wells in Texas and New Mexico, and this has led to the hope that deposits might be found here comparable with those in Stassfurt. Unless new deposits or new sources of potassium salts are found, the indications are that the United States will continue to obtain its main supply from Germany and France.

**Preparation and properties.** Potassium is prepared by methods similar to those used in the preparation of sodium, but the process is more difficult to carry out. It is more active than sodium; otherwise the properties of the two metals are closely parallel.

In a general way the compounds of potassium are similar to the corresponding ones of sodium and therefore will not be discussed in such detail.

**Potassium hydroxide (caustic potash) (KOH).** Potassium hydroxide is prepared by methods exactly similar to those used in the preparation of sodium hydroxide, and it closely resembles this compound in both physical and chemical properties. It is not now used to any very great extent, having been replaced by the cheaper sodium hydroxide.

**Action of the halogen elements on bases.** We have seen that when chlorine is passed into a solution of potassium hydroxide a reaction takes place (p. 312), and that the nature of the reaction varies according to the temperature of the solution. If the solution is cold, potassium hypochlorite and potassium chloride are formed, according to the following equation:



If the solution is hot, however, potassium chlorate and potassium chloride are formed:



This reaction is a general one between the halogen elements and the soluble bases. Thus, in place of chlorine in the above equations one may substitute bromine or iodine; also, in place of the potassium hydroxide one may substitute sodium hydroxide or calcium hydroxide. It is possible by this reaction to prepare a number of important compounds. It does not follow, however, that this method of preparation of any particular compound is necessarily the most economical one.

**Potassium halides.** The three compounds, potassium chloride (KCl), potassium bromide (KBr), and potassium iodide (KI), are often termed collectively the *potassium halides*. Of these compounds *potassium chloride* is the most familiar, since it is found in such large quantities in the Stassfurt deposits. The mineral *sylvite* is nearly pure potassium chloride. The salt is obtained not only from sylvite but also from carnallite. In its general properties potassium chloride resembles sodium chloride. It is used in the preparation of nearly all other

potassium salts and as a fertilizer. *Potassium bromide* is prepared by the action of bromine upon a hot solution of potassium hydroxide (see preceding paragraph). *Potassium iodide* is prepared by the same method, with the substitution of iodine for bromine. Both the iodide and the bromide are used in photography and in medicine.

**Potassium chlorate ( $\text{KClO}_3$ ).** This salt is formed when chlorine acts upon hot solutions of potassium hydroxide:



It will be noted, however, that the yield is very small, six molecules of the hydroxide giving but one of the chlorate. Commercially the yield is greatly improved by generating the chlorine and potassium hydroxide by the electrolysis of potassium chloride under such conditions that they react to form the chlorate according to the above equation. By continuing the process all the chloride is finally converted into the chlorate.

Potassium chlorate is an excellent oxidizing agent and, like sodium chlorate, is used in the manufacture of munitions, fireworks, and matches; indeed, it is preferred to sodium chlorate, since the latter compound is deliquescent.

**Potassium nitrate (saltpeter) ( $\text{KNO}_3$ ).** This salt is found native in some regions where the climate is hot and dry, being formed by the decay of nitrogenous organic matter in the presence of earthy material containing potassium. Saltpeter was formerly made by imitating these conditions. It is now prepared by the action of sodium nitrate upon potassium chloride (the former compound being obtained from Chile and the latter from the Stassfurt deposits):



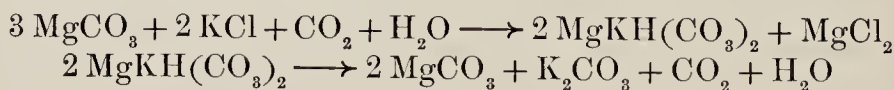
The reaction depends for its success upon the apparently insignificant fact that sodium chloride is almost equally soluble in cold and in hot water. All four compounds represented in the equation are rather soluble in cold water, but in hot water sodium



chloride is far less soluble than the other three. When hot saturated solutions of sodium nitrate and potassium chloride are brought together, sodium chloride precipitates and can be filtered off, leaving potassium nitrate in solution together with some sodium chloride. When the solution is cooled, potassium nitrate crystallizes out, leaving small quantities of the other salts in solution.

Potassium nitrate is an excellent oxidizing agent, and its chief use is in the manufacture of gunpowder. For this purpose it is preferable to sodium nitrate, since the latter tends to absorb moisture, and powder made from it, if exposed to air, soon becomes moist and unfit for use. Small quantities of the nitrate are also used in medicine and as a preservative for meats, especially for corned beef.

**Potassium carbonate ( $K_2CO_3$ ).** This compound can be prepared from potassium chloride by the Leblanc process, just as sodium carbonate is prepared from sodium chloride. The Solvay process will not work, however, since potassium bicarbonate is too soluble and hence will not separate like the sodium bicarbonate. Commercially potassium carbonate is prepared from the mineral *sylvite* (p. 440) according to the reactions indicated in the following equations:



Potassium carbonate is used principally in the manufacture of glass.

**Other salts of potassium.** Among the other salts of potassium frequently met with are the *sulfate*,  $K_2SO_4$ ; the *acid sulfate*,  $KHSO_4$ ; the *acid sulfite*,  $KHSO_3$ ; and the *cyanide*,  $KCN$ . They are all white solids and closely resemble the corresponding compounds of sodium.

**Sodium compounds and potassium compounds contrasted.** The compounds of sodium and potassium are not only alike in composition but so nearly resemble each other in properties that, for the great majority of uses, it is immaterial which of the two corresponding

compounds is employed. Thus, for an operation requiring a strong base we may employ either sodium hydroxide or potassium hydroxide. Other things being equal, the cheaper compound will be selected. Since the natural compounds of sodium are much more readily available than those of potassium, we should expect the compounds of sodium to be less expensive and therefore more generally used, and this is true. It must be remembered, however, that the cost of a compound depends not only on the availability of raw materials but also upon the cost of the operation required to produce the compound. Now it is generally true that the salts of sodium are much more soluble than those of potassium. They are, therefore, often more difficult to obtain in a pure state, since their greater solubility makes it more difficult to purify them. For this reason potassium chlorate is more readily obtained pure than sodium chlorate. Again, the compounds of sodium are more deliquescent than those of potassium, and this difference sometimes influences the choice. Thus, potassium nitrate is used for making gunpowder in preference to the cheaper sodium nitrate.

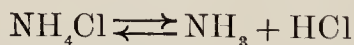
Furthermore, an examination of the formulas of the compounds of sodium and potassium will show that more of the former are hydrates than of the latter, and this may enter into the choice of compounds.

### COMPOUNDS OF AMMONIUM

**Properties.** As explained in Chapter XVIII, when ammonia is passed into water, the two unite to form the base ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), and when this base is neutralized with acids, ammonium salts are formed. Since the ammonium radical ( $\text{NH}_4$ ) is univalent, ammonium salts resemble those of the alkali metals in formulas; they also resemble the latter salts in their chemical properties and may be conveniently described in connection with them. They all volatilize upon being heated, most of them being decomposed in the process. When heated with an aqueous solution of sodium hydroxide, they evolve ammonia (p. 220). Since the ammonia can be easily recognized, the reaction serves for the detection of the presence of ammonium compounds.

**Occurrence and uses.** Small quantities of ammonium compounds are found in the soil. They are being continually absorbed by growing plants, but are returned to the soil again in the process of decay. They are also found in sea water and in some volcanic regions. Larger quantities are found in the Stassfurt deposits. Commercially ammonium compounds are obtained in the United States largely from the ammoniacal liquors produced in the manufacture of coke and coal gas (pp. 377, 378). Synthetic processes, however, are coming into use more and more for the preparation of ammonia, from which the ammonium salts are easily prepared by treatment with the appropriate acid. The Haber ammonia process has already been discussed, and other processes will be described in a later chapter. The chief use of the ammonium salts is for a fertilizer. Other uses will be indicated in the discussion of the individual salts.

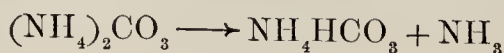
**Ammonium chloride (sal ammoniac) ( $\text{NH}_4\text{Cl}$ ).** This salt, commonly known as *sal ammoniac*, is a white solid. When heated it partly decomposes into ammonia and hydrogen chloride, which recombine as the temperature falls:



This salt is used in soldering, since the hydrogen chloride evolved by the heat removes the oxide from the surface of the metals. It is also used in making dry cells, in medicine, and as a chemical reagent.

**Ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ).** This salt resembles the chloride very closely and, being cheaper, is used in place of it when possible. It is used in large quantities as a fertilizer, the nitrogen which it contains being a very valuable food for plants.

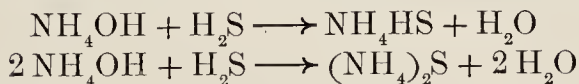
**The carbonates of ammonium.** Both the normal carbonate,  $(\text{NH}_4)_2\text{CO}_3$ , and the acid carbonate,  $\text{NH}_4\text{HCO}_3$ , are white solids, readily soluble in water. The normal carbonate slowly decomposes into the acid carbonate, evolving ammonia:



**Commercial ammonium carbonate.** When a mixture of powdered limestone and either ammonium chloride or ammonium sulfate is heated, there is formed a sublimate known as *commercial ammonium carbonate*. This is made up of ammonium bicarbonate and ammonium carbamate. The latter is the ammonium salt of *carbamic acid* and has the formula  $\text{NH}_4 \cdot \text{CO}_2\text{NH}_2$ . When ammonia is passed into a solution of the sublimate in water, normal ammonium carbonate is formed:



**Ammonium sulfides.** When hydrogen sulfide is passed into aqua ammonia, there is obtained a solution containing ammonium acid sulfide ( $\text{NH}_4\text{HS}$ ) and ammonium sulfide ( $(\text{NH}_4)_2\text{S}$ ):



The normal sulfide, however, is almost completely hydrolyzed in solution, forming the acid sulfide and ammonium hydroxide.

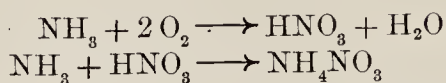
**Ammonium polysulfide.** When exposed to the air ammonium sulfide slowly decomposes, and the sulfur liberated in the process combines with the compounds present, forming different sulfides, such as  $(\text{NH}_4)_2\text{S}_2$  and  $(\text{NH}_4)_2\text{S}_3$ , or, in general,  $(\text{NH}_4)_2\text{S}_x$ . The resulting solution is yellow and is termed *yellow ammonium sulfide* or *ammonium polysulfide*.

**Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ).** This salt may be prepared by the action of nitric acid upon ammonium hydroxide. It is used in the preparation of nitrous oxide (p. 234) and as a constituent of certain explosives. For example, the explosive *ammonal*, so largely used in the World War, consisted of ammonium nitrate and powdered aluminum. Sometimes varying quantities of potassium nitrate and charcoal are added.

The nitrate plant erected during the World War, at Muscle Shoals, Alabama, had a capacity of 300 tons of ammonium nitrate daily. In this plant ammonia was made from atmospheric nitrogen by a process to be described later (see cyanamide) and oxidized



to nitric acid (p. 228). The resulting acid was then combined with more ammonia to form ammonium nitrate:



**Flame reactions.** There are several metals which, when volatilized in a colorless flame, such as that of a Bunsen burner, impart a characteristic color to the flame. Thus, sodium (or any of its compounds that will volatilize in the heat of the

flame) imparts to the flame a strong yellow color. Potassium and its compounds color the flame a pale violet, and lithium colors it a deep crimson red.

Advantage is taken of these facts in testing for the presence of the elements in different substances. The test is best made by using a platinum

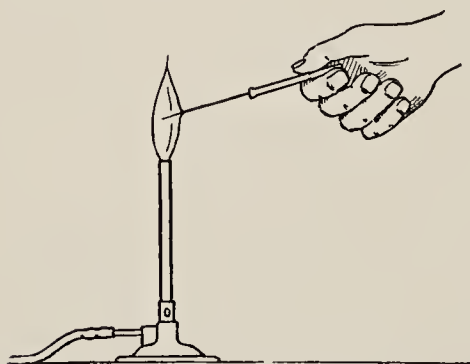


FIG. 183. Method of making a flame test

wire one end of which is fused into a piece of glass tubing that serves as a handle. The other end of the wire is dipped into water and rubbed in the substance to be tested (or dipped into a concentrated solution of the substance), and the wire with the adhering particles is held in the outer edge of the base of the Bunsen flame (Fig. 183).

**The spectroscope.** The spectroscope (Fig. 185) is an instrument used for the examination of light from various sources. It was invented by Bunsen (Fig. 178) and Kirchhoff and in their hands led to the discovery of rubidium and cesium. It has been of the greatest service, leading to many remarkable discoveries, so that a brief description of the principle upon which the instrument is constructed and the principal method employed in its use will not be out of place here.

**Detailed description.** When a beam of light passes through a triangular prism of glass, it is bent out of its course and emerges at a decided angle with its original direction, as shown in Fig. 184. Ordinary light is made up of many different wave lengths, and each one is deflected, or *refracted*, to a different degree, so that the various colors of which the light is composed are spread out in a series, the red being the least refracted, the violet the most so. A beam of *white* light gives a continuous series of colors, from red through orange, yellow, green, blue, to violet, called a *continuous spectrum*. The spectrum of any *colored* light is not continuous, but shows merely those colors of which the light is composed.

That these colors may be made as distinct and sharply separated as possible, the light should shine upon the prism through a very narrow slit in a screen, arranged so as to be parallel with the axis of the prism. The colors will then be a series of narrow lines, each an image of the slit, spread out parallel with each other. An instrument, the essential parts of which are a prism, a screen provided with a narrow slit, and lenses for focusing the light upon the slit and for viewing the spectrum, is called a *spectroscope*, or *spectrometer*. Fig. 185 represents a simple form of such a spectroscope, the slit being seen at the end of the tube *B*. When we look into the eyepiece *A*, the spectrum of the flame is seen as a series of bright lines on a dark field. The tube *C* contains a scale which is also seen when we look into the eyepiece. Any incandescent solid, such as a glowing platinum wire, glowing carbon, or an incandescent lamp, gives a continuous spectrum, all wave lengths of light being represented. Light from volatilized salts and glowing gases gives an interrupted or line spectrum, characteristic of the particular substance giving rise to the light.

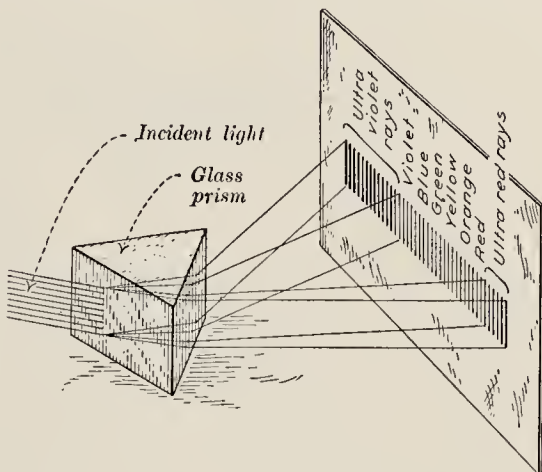


FIG. 184. Diagram showing how a beam of white light is separated into its constituents

Each element has its characteristic spectrum. The spectroscope, therefore, not only enables us to detect the presence of known elements, but, through the appearance of new lines on the spectra of different materials, leads to the discovery of new elements. It is interesting to recall that lines in the solar spectrum indicated the existence of an element unknown on the earth at that time, and the name *helium* was given to this element. Thirty years later the element was found in the earth's atmosphere (p. 91).

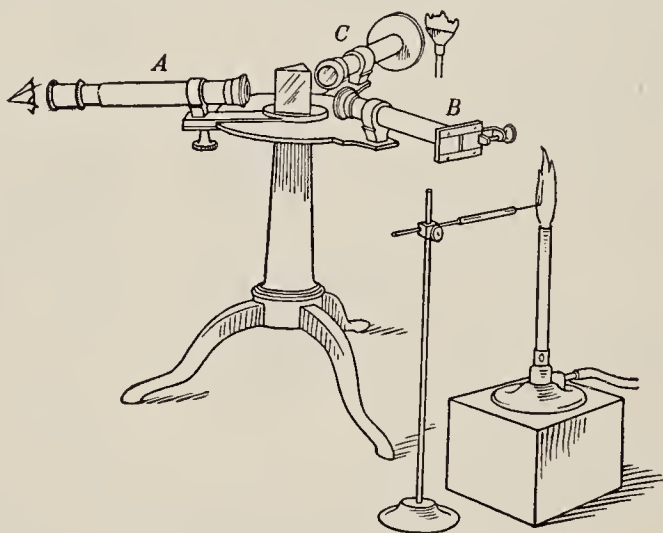
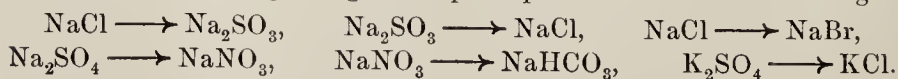


FIG. 185. A simple spectroscope

There are a number of ways in which the spectroscope may be used. In the case of substances easily volatilized it is only necessary to dip a platinum wire into some of the substance or its concentrated solution, heat the wire in a Bunsen flame, and examine the resulting flame as shown in Fig. 185. For detailed information concerning the spectroscope and its uses the student is referred to more advanced treatises.

#### EXERCISES

1. What is an alkali? Can a metal itself be an alkali?
2. Write equations showing how the following changes may be brought about, giving the general principle involved in each change:



3. What carbonates are soluble?

4. State the conditions under which the reaction represented by the following equation can be made to go in either direction:



5. Account for the fact that solutions of sodium carbonate and potassium carbonate are alkaline.

6. What nonmetallic element is obtained from the deposits of Chile saltpeter?

7. Write equations for the preparation of potassium hydroxide by three different methods.

8. What would take place if a bit of potassium hydroxide were left exposed to the air?

9. Write equations for the preparation of potassium sulfate; of potassium-acid carbonate.

10. Write the equations showing how ammonium chloride, ammonium sulfate, ammonium carbonate, and ammonium nitrate may be prepared from ammonium hydroxide.

11. Write an equation to represent the reaction involved in the preparation of ammonia from ammonium chloride.

12. What substances already studied are prepared from the following compounds: ammonium chloride; ammonium nitrate; ammonium nitrite; sodium nitrate; sodium chloride?

13. Write equations for the preparation of potassium iodide and potassium bromide.

14. How could you distinguish between potassium chloride and potassium iodide? between sodium chloride and ammonium chloride? between sodium nitrate and potassium nitrate?

15. What are the relative advantages of sodium chlorate and potassium chlorate as oxidizing agents?

16. Write the names and formulas for the different compounds that may be formed by the action of the halogen elements on the soluble bases.

17. Supposing concentrated hydrochloric acid (den. = 1.2) to be worth 8 cents a pound, what is the value of the acid generated in the preparation of 1 ton of sodium carbonate by the Leblanc process?

18. What weight of sal soda can be prepared from 1 kg. of anhydrous sodium carbonate?

19. What weight of carnallite would be necessary in the preparation of 1 ton of potassium carbonate?



## CHAPTER XXXIII

### SOAP; GLYCERIN; EXPLOSIVES

**Introductory.** At first thought one might wonder why three products so different from each other as soap, glycerin, and explosives should be brought together for study in the same chapter. The grouping is a natural one industrially, however, for glycerin is a by-product in the manufacture of soap, and nitroglycerin, one of the most powerful explosives, is prepared from glycerin and stands in a general way as a type of an explosive compound. It is convenient, therefore, in a very brief description of these products, to include all three in the same chapter.

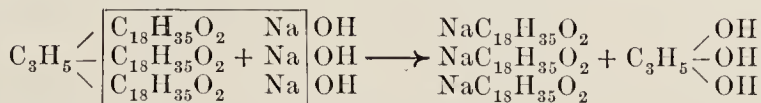
**Composition of soap, and materials used in its preparation.** Soap is chiefly a mixture of the sodium or potassium salts of oleic, palmitic, and stearic acids (p. 415). The essential materials used in the preparation of soap are as follows:

1. ***Fat or oil.*** As shown on page 415, fats and oils are largely mixtures of olein, palmitin, and stearin. The cheaper grades of these are used in making soap. Those commonly employed are a low grade of animal fat (tallow and grease) and the cheaper vegetable oils, such as cottonseed oil, coconut oil, and palm oil.

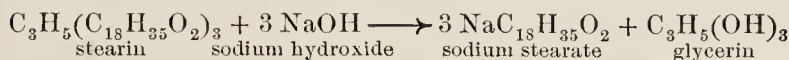
2. ***Alkali.*** The alkali used is the hydroxide of either sodium or potassium. Sodium hydroxide is nearly always used, since it gives a hard soap, while potassium hydroxide gives a soft soap. Other bases, such as calcium hydroxide, are unavailable, since they yield insoluble soaps.

**Reaction taking place in the preparation of soap.** When the fat or oil and alkali are heated together under proper conditions, the olein, palmitin, and stearin present in the fat decompose,

forming glycerin, together with sodium oleate, sodium palmitate, and sodium stearate. A mixture of these three salts constitutes ordinary soap. The reactions may be illustrated by the following equation, which represents the change taking place when stearin is heated with sodium hydroxide:



or, expressed in more condensed form,



In this reaction the fat is said to be *saponified*, and the process is known as *saponification*.

#### Commercial manufacture of soap.

The oil or melted fat is poured into large iron kettles together with a solution of sodium hydroxide containing about one fourth of the amount of alkali necessary to saponify the fat. As a rule the kettles (Fig. 186) are very large, 500,000 lb. or more of soap being made in some of them in a single heating. They are provided with coils of steam pipe for heating the liquid. The fat and alkali are stirred by forcing live steam into the bottom of the mixture. As the heating continues, the remainder of the alkali is added. The reaction is complete in about one day. The soap is then in the form of a colloidal dispersion in the liquids present. In order to separate the soap, common salt is added (p. 357),—a process known as “salting out.” After the salt is added and the mixture heated, the soap rises to the top of the liquid, or *spent lye*, as it is called.

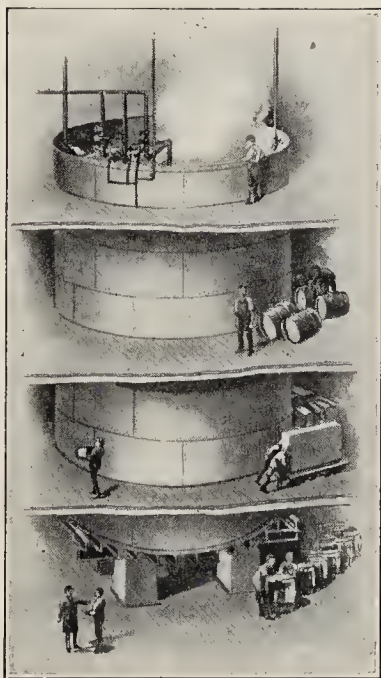
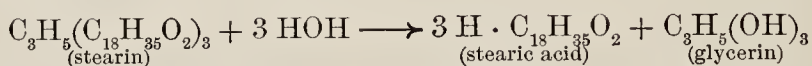


FIG. 186. View of a kettle used in the manufacture of soap

The soap so obtained is purified by washing and settling processes and then run into a mixing machine (crutcher). Here it is mixed with any appropriate material which it is desired to add, such as perfume, borax, sodium silicate, or sodium carbonate. It is then run into large molds called *frames* to harden, after which it is cut and pressed into cakes of the desired size. The glycerin formed in the reaction is concentrated by evaporation and refined by distillation.

Large quantities of laundry soap, as well as candles, are made from low-grade fats as follows: The fats are first heated with appropriate reagents which bring about the following change (using stearin as an example):

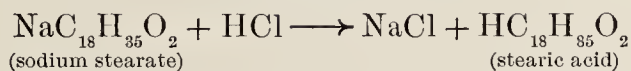


The resulting fatty acids are then separated and purified by distilling them in vacuo in a current of steam. The purified fatty acids are then changed into soap by neutralizing them with sodium carbonate, or into candle stock by subjecting them to pressure which squeezes out the liquid acids, leaving the stearic acid, from which the candles are then made.

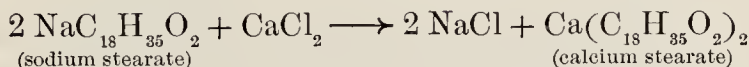
**Varieties of soap.** Transparent soaps are ordinarily made by dissolving soap in alcohol and adding from 15 to 25 per cent of sugar. The solution is filtered, and the excess of alcohol removed by distillation. True Castile soaps are made of olive oil. The color of mottled soaps is produced by the addition of ferrous sulfate, Prussian blue, or some similar pigment. Floating soaps owe their lightness to bubbles of air. Naphtha soaps contain about 5 per cent of petroleum naphtha. Scouring soaps contain from 5 to 10 per cent of soap and from 80 to 90 per cent of some abrasive material such as fine sand or volcanic ash. Sometimes a small percentage of sodium carbonate is also present. Soap powders are, as a rule, normal sodium phosphate (p. 437) or sodium carbonate, mixed with from 10 to 25 per cent of ground soap.

**Properties of soap.** When soap is added to soft water, it apparently dissolves. Experiments show, however, that most of the soap is present in the form of a colloidal dispersion. Some hydrolysis takes place so that the liquid is basic in character. If an acid, such as hydrochloric acid, is added to

this solution, the organic acids are liberated from their salts and are precipitated in the form of white insoluble solids:



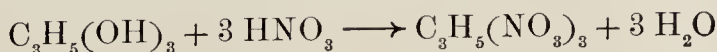
The calcium and magnesium salts of oleic, palmitic, and stearic acids are insoluble in water and do not form emulsions, so that they are precipitated when a calcium or magnesium compound is added to an aqueous solution of soap:



It is due to this fact that soaps do not lather with hard waters (p. 517), but form a curdy precipitate, since such waters always contain salts of calcium and magnesium in solution.

**Cleansing action of soap.** There has been a great deal of study and discussion in the effort to find out the true explanation of the cleansing action of soap, and much uncertainty still remains. Attention has been called to the property possessed by soap of aiding in the formation of emulsions (p. 358), and the cleansing action of soap is thought to be due primarily to this property. When soap is rubbed on the skin, any fatty substances present are emulsified by the soap and washed away. Soap also seems to have a selective adsorption for different forms of grease and dirt (p. 356). The soap in water is in the form of a colloid, and this colloid adsorbs the dirt and grease and thus removes it. It is probable that the efficiency of soap as a cleansing agent is due to a number of properties, among which the two given above are the chief ones.

**Glycerin ( $\text{C}_3\text{H}_5(\text{OH})_3$ ).** This is a colorless, oily liquid having a sweet taste. It is formed whenever a fat is acted upon by an alkali and consequently is a by-product in the manufacture of soap. Nitric acid acts upon it, forming *glyceryl nitrate*, as indicated in the following equation:





In actually carrying out this reaction a mixture of nitric and sulfuric acid is always used; the sulfuric acid aids in the reaction by absorbing the water produced. It will be noted that the reaction is exactly similar to that of nitric acid upon a base, so that glyceryl nitrate is really a salt of nitric acid. Glyceryl nitrate is a slightly yellowish oil. It is a powerful explosive and is the chief constituent of the explosive known as *nitroglycerin*. The chief use of glycerin is in the preparation of this product.

**Utilization of garbage.** Many cities now treat their garbage in such a way that it becomes a source of revenue rather than expense. The garbage is first heated with steam and hot water. This causes the oils and fats to collect as a liquid on the top of the hot water so that they can easily be removed. The residue makes a valuable fertilizer, while the fats and oils are used in making candles, soap, and glycerin.

**Explosives.** An explosion is caused by a very rapid chemical reaction which results in the formation of a large volume of gas from a comparatively small volume of reacting substances. The greater the volume change and the more rapidly it is produced, the more violent the explosion.

For a brief discussion we may divide explosives into two groups: namely, (1) gunpowder and (2) nitro-explosives.

1. **Gunpowder.** Gunpowder is an intimate mixture of potassium nitrate, charcoal, and sulfur. When ignited by a spark it burns explosively, forming a number of products, some of which are gases, while others are solids. The gases constitute about 50 per cent by weight of the total products and consist principally of carbon monoxide, carbon dioxide, and nitrogen, while the principal solids formed are potassium carbonate, potassium sulfate, and potassium sulfide.

2. **Nitro-explosives.** These are compounds of carbon, hydrogen, oxygen, and nitrogen. When they are exploded, the carbon and hydrogen unite with the oxygen to form oxides of carbon and water vapor, while the nitrogen is liberated in the free state. These explosives are all made by the action of a mixture of nitric

and sulfuric acid upon certain compounds, the name of the explosive ordinarily indicating the compound used. The most important of the nitro-explosives are given below :

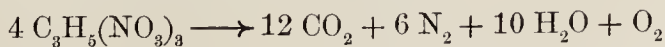
(a) *Nitrocellulose* (approximate composition,  $C_6H_7O_2(NO_3)_2$ ). This substance (p. 398) is a far more powerful explosive than gunpowder. If ignited, it will, under ordinary conditions, burn quietly. If subjected to a sudden shock (such as may be produced by the explosion of a small percussion primer), the nitrocellulose



FIG. 187. Powder grains for large guns (natural size)

decomposes with enormous violence. The products of the decomposition are all colorless gases ; hence the use of this explosive in making *smokeless* gunpowder. When used for this purpose it is necessary to modify the pure material somewhat, as otherwise the violence of the explosion would shatter any firearms in which the powder was used. This is done by mixing nitrocellulose with sufficient alcohol and ether to form a jelly. This is then molded into the form of rods (grains), with a number of perforations through the rods. The size of the grains varies with the size of the guns in which the powder is used. Fig. 187 shows the form of the grains used in some of the large guns of our navy.

(b) *Nitroglycerin* ( $C_3H_5(NO_3)_3$ ). This compound (p.456) resembles nitrocellulose in the violence of its explosive effects. The changes taking place in its decomposition are represented in a general way by the following equation :



One volume of nitroglycerin yields on explosion about 1300 volumes of gas, which is expanded by the heat of the reaction to over 10,000 volumes. Pure nitroglycerin is very dangerous because

of the ease with which it is set off. Large quantities are used in making *dynamite*, and in this form it is not exploded so readily by jarring and can be transported with less danger. Ordinary

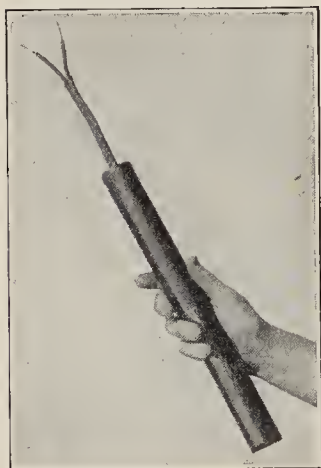


FIG. 188. A stick of dynamite

dynamite (Fig. 188) consists of a mixture of sodium (or ammonium) nitrate, nitroglycerin, and wood pulp, the latter acting like a sponge to absorb the nitroglycerin. When stored, the compounds present in dynamite are apt to decompose slightly, giving rise to an acid which may cause the dynamite to explode; hence a small percentage of calcium carbonate or some similar compound is added to the mixture to neutralize any acid as fast as formed. *Gelatin dynamite* consists of nitrocellulose and nitroglycerin mixed together to form a jelly. It is a very powerful explosive, since it contains no inert material.

(c) *Trinitrotoluene* ( $C_7H_5(NO_2)_3$ ) is the explosive commonly known as **T.N.T.** It is a white solid but colors on exposure to air. It is too powerful to be used in guns but is especially adapted to use in bombs and torpedoes. The depth bombs used in the World War for destroying submarines contained about 300 lb. each of **T.N.T.**

(d) *Picric acid* or *trinitrophenol* ( $C_6H_2OH(NO_2)_3$ ). This is a yellow solid (p. 408) and was the favorite explosive of the French in the World War. Large quantities were made in the United States and shipped to France.

### EXERCISES

1. In former years (and even now to a limited extent) farmers made their own soaps by heating refuse fats with a liquid obtained by treating wood ashes with water. (a) What is the alkali used? (b) What kind of soap (hard or soft) would be formed by this method?

2. Why not use calcium hydroxide for the alkali in soap-making?

3. What is the significance of the word *glycerin*?

4. Give the chemical reactions involved in making glycerin from garbage.

5. What changes take place when a solution of soap is treated with each of the following reagents: (a) sodium chloride; (b) dilute sulfuric acid; (c) magnesium chloride?

6. Should you expect gunpowder to be as violent an explosive as nitroglycerin?

7. Why not use sodium nitrate in place of potassium nitrate in making gunpowder?

8. Why are some gunpowders smokeless and others not?

9. Why not use dynamite as an explosive in firing cannons?

10. Why will gas which burns quietly in a stove explode if it is allowed to escape into a room and is then ignited?

11. The carbon and hydrogen in T.N.T. tend to form carbon dioxide and water respectively when the compound explodes. Is there sufficient oxygen in the explosive to combine with all the carbon and hydrogen present?

12. When bombs filled with T.N.T. explode, dense clouds of black smoke are formed. Account for this result.

13. (a) 100 kg. of stearin would require how many kilograms of sodium hydroxide to convert it into soap? (b) What weight of glycerin would be formed?

14. Nitroglycerin is an oily liquid of density 1.6. (a) Upon the assumption that the equation given under (b), p. 457, correctly represents the reaction taking place when nitroglycerin explodes, what volume of gas measured under standard conditions would be formed by the explosion of 1 kg. of nitroglycerin? (b) What volume would this gas occupy if the temperature of the gas were raised to  $2000^{\circ}$  by the heat generated in the explosion (omit in the calculations the water formed in the explosion)?



## CHAPTER XXXIV

### THE ALKALINE EARTH METALS

	ATOMIC WEIGHT	DENSITY	MELTING POINT	FIRST PREPARED
Calcium (Ca) . . . . .	40.07	1.55	810°	Davy, 1808
Strontium (Sr) . . . . .	87.63	2.60	800°(?)	Davy, 1808
Barium (Ba) . . . . .	137.36	3.5	850°	Davy, 1808

**The family.** Calcium, strontium, and barium are known as the *alkaline earth metals*. Together with radium they constitute one of the families in Group II of the periodic table. While radium closely resembles barium, it is more convenient to discuss it in connection with uranium, to which it bears a peculiar relation. The term *alkaline earths* was originally applied to the oxides of these metals because they bore some resemblance both to the alkalis and to the earths, the latter being a general term for such oxides as those of iron and aluminum. As in the case of the alkalis, the alkaline earths were thought to be elementary in character until 1808, when Davy (Fig. 76) succeeded in decomposing them, just as he had decomposed the alkalis.

In a lecture delivered on June 30, 1808, before the English Royal Society, Davy refers to his discovery as follows: "The evidence for the composition of the alkaline earths is then of the same kind as that for the composition of the common metallic oxides; and the principles of their decompositions are precisely similar. . . . These new substances will demand new names; and on the same principles as I have named the bases of the fixed alkalis I shall venture to denominate the metals from the alkaline earths barium, strontium, calcium. . . ."

The alkaline earth metals are light, active elements. They form compounds in which the metal acts as a bivalent element. Unlike the alkali metals their normal carbonates, phosphates, and silicates are insoluble in water. Barium sulfate is also insoluble, while the sulfates of calcium and strontium are but sparingly soluble.

### CALCIUM

**Properties and occurrence.** We are all more or less familiar with the building stone known as *marble*, as well as with the common rock *limestone*, from which we prepare ordinary lime so largely used in making such products as mortar and plaster. Both marble and limestone are composed chiefly of the carbonate of the metal calcium ( $\text{CaCO}_3$ ), marble being the purer form and crystalline in character. When calcium carbonate is treated with hydrochloric acid, calcium chloride is formed, — a reaction which is used in preparing carbon dioxide (p. 141). By the electrolysis of the chloride the metal itself is liberated.

Calcium resembles sodium and potassium in being a light, silver-white metal. Like these metals also it decomposes water, forming the hydroxide of the metal and liberating hydrogen. It is much harder than either sodium or potassium, however, and melts at a much higher temperature ( $810^\circ$ ). When ignited it burns in the air with great brilliancy.

Calcium is one of the abundant elements. Its compounds are found in large quantities in various regions. Its most abundant form is the carbonate. The important calcium-bearing minerals are the following:

Calcite . . . . .	$\text{CaCO}_3$	Wollastonite . . .	$\text{CaSiO}_3$
Phosphorite . . . .	$\text{Ca}_3(\text{PO}_4)_2$	Gypsum . . . . .	$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$
Fluorite . . . . .	$\text{CaF}_2$	Anhydrite . . . .	$\text{CaSO}_4$

Our bodies contain about 2 per cent of calcium, chiefly in the form of calcium phosphate, which is the principal mineral constituent of our bones.

**Preparation.** Calcium is prepared commercially by the electrolysis of the melted chloride in the following way:

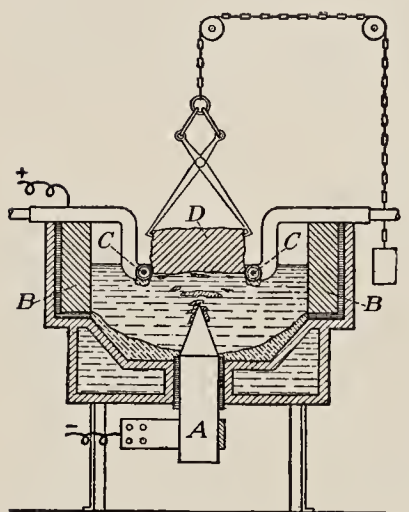


FIG. 189. Diagram of cell used in the preparation of calcium by electrolysis

**Apparatus.** The apparatus consists of a cylindrical iron vessel (Fig. 189) through the bottom of which extends the iron cathode *A*. The anodes *B, B*, several in number, are placed about the sides of the vessel. The calcium separates in a molten condition at the cathode *A* and rises in the form of globules to the lower surface of a solid stick of calcium *D*, suspended above the cathode. There it is chilled by a water-cooling device *C, C*, and adheres to the stick of calcium, which is slowly raised as it increases in length.

**Calcium carbonate ( $\text{CaCO}_3$ ).** Enormous quantities of calcium carbonate occur in nature. *Limestone* is the most abundant form and sometimes constitutes whole mountain ranges. Limestone is never pure calcium carbonate but contains variable percentages of magnesium carbonate, clay, silica, and compounds of iron. Pearls, coral, and various shells are largely calcium carbonate. *Calcite* is a very pure crystalline form and is often found in large, transparent crystals (belonging to the hexagonal system) called *Iceland spar* (Fig. 190). *Marble* is composed of very small calcite crystals. Calcium carbonate also crystallizes in the rhombic system, as in the mineral *aragonite*.

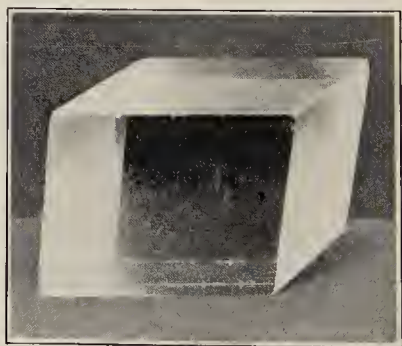
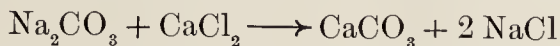


FIG. 190. Crystal of calcite

In the laboratory pure calcium carbonate can be prepared by treating a soluble calcium salt with a soluble carbonate:

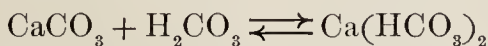


When prepared in this way it is a soft, white powder often called *precipitated chalk* and is much used as a polishing powder (tooth powder).

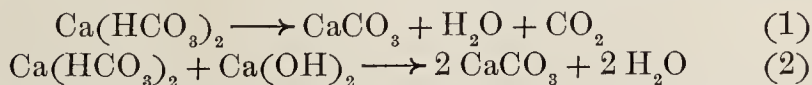
The natural varieties of calcium carbonate find many uses, as in the preparation of lime and in metallurgical operations, especially in blast furnaces; in the manufacture of soda and glass; for building stone; and for ballast for roads.

**Dimorphous compounds.** Calcium carbonate is an example of a *dimorphous* compound; that is, it crystallizes in two different allotropic forms. Thus, calcite crystals belong to the hexagonal system (see Appendix), while aragonite forms crystals belonging to the rhombic system.

**Calcium acid carbonate ( $\text{Ca}(\text{HCO}_3)_2$ ).** Calcium carbonate is almost insoluble in pure water. It readily dissolves, however, in water which holds carbon dioxide in solution. This is due to the fact that the carbonate combines with the carbonic acid present in the water and forms calcium acid carbonate, which is soluble:



The resulting acid carbonate exists only in solution, since it is unstable and decomposes easily into the normal carbonate. This change can be brought about either by heating (equation (1)) or by the addition of calcium hydroxide (equation (2)):



The normal calcium carbonate, being insoluble, separates from the solution as fast as formed. The reaction with calcium hydroxide is utilized in the softening of water. The methods for doing this will be discussed in a later chapter.



**Formation of caves.** Natural waters always contain more or less carbon dioxide in solution. In the case of certain underground waters the amount of carbon dioxide is comparatively large, being held in solution by pressure. Such waters have a marked solvent action upon limestone, dissolving both the calcium carbonate and the magnesium carbonate. In certain localities this solvent action, continued through geological ages, has resulted in the formation, in limestone rock, of large caves such as the Mammoth Cave



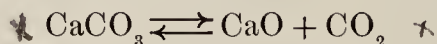
FIG. 191. View in a cave showing formation of stalactites and stalagmites

in Kentucky. Sometimes water trickling through the roofs of these caves evaporates, leaving a deposit of calcium carbonate, which, as the process continues, often forms icicle-shaped masses known as *stalactites*; or the water may drip upon the floor of the cave, building up similar masses known as *stalagmites* (Fig. 191).

#### Calcium oxide (lime) (CaO).

Pure calcium oxide can be prepared by burning calcium in oxygen or by heating the nitrate or the carbonate. The more or less impure oxide, known commercially as *lime*

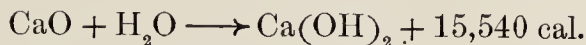
or *quicklime*, is prepared on a large scale by heating limestone, which is chiefly calcium carbonate ( $\text{CaCO}_3$ ). When heated the calcium carbonate decomposes according to the following equation :



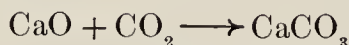
The reaction is reversible, so that in manufacturing practice the decomposition is effected under conditions that will conduct away the carbon dioxide as fast as it is formed.

Ordinary lime is a white amorphous substance. When heated intensely, as in the oxyhydrogen flame, it gives a brilliant light. It melts only in the heat of the electric furnace. Water acts

upon lime with the evolution of considerable heat (whence the name *quicklime*, or *live lime*), the process being called *slaking*. The equation is



Because of its affinity for water it is used for drying gases. It also absorbs carbon dioxide, forming the carbonate



Lime exposed to air is therefore gradually converted into the hydroxide and the carbonate and will no longer slake with water. It is then said to be *air-slaked*. Lime is produced in enormous quantities for use in making calcium hydroxide.

#### Commercial production of lime.

Lime is made by heating limestone in large, chimneylike furnaces called *limekilns*. A vertical section of a modern limekiln is shown in Fig. 192. The kiln is about 50 ft. in height. The fire boxes, or furnaces (*B, B*), are built around the lower part, and lead into the central stack. Limestone is added at the top of the kiln, as shown in *A* (Fig. 192). The hot products of combustion are drawn up through the kiln, and the limestone is gradually decomposed by the heat.

The bottom of the furnace is so constructed that a current of air

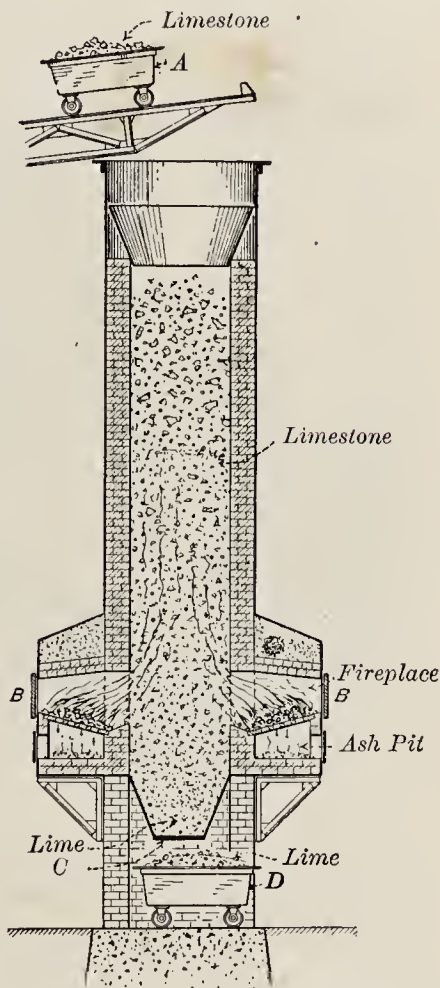


FIG. 192. A vertical section of a limekiln

is drawn in at *C*. This serves the purpose of cooling the hot lime at the base of the furnace, of furnishing heated oxygen for the combustion, and of removing the carbon dioxide from the kiln. The lime is dropped into cars *D* run under the furnace. Usually a number of these kilns are operated together, as shown in Fig. 193.

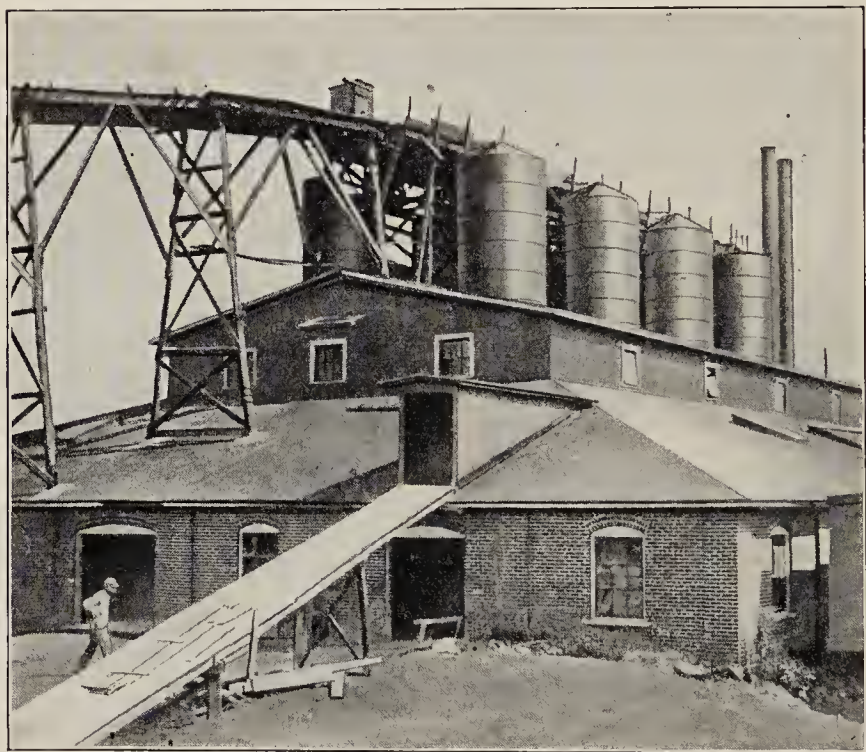
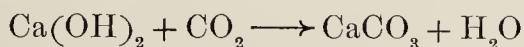


FIG. 193. A group of limekilns operated together

**Calcium hydroxide (slaked lime) ( $\text{Ca}(\text{OH})_2$ ).** This compound is prepared by adding water to lime, as explained above. When pure it is a light, white powder. It is sparingly soluble in water. Moreover, its solubility diminishes slightly with rise in temperature. Thus, 1 liter of water at  $10^\circ$  dissolves 1.76 g. of the hydroxide, while at  $100^\circ$  the same volume of water dissolves only 0.77 g. The aqueous solution is called *lime-water*. Owing to its cheapness calcium hydroxide is used in the industries whenever an alkali is desired. It is used in the

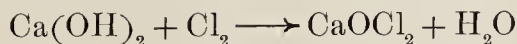
preparation of ammonia, bleaching powder, and the hydroxides of sodium and potassium. It is also used to remove sulfur compounds and carbon dioxide from coal gas, to remove the hair from hides in making leather, and for making mortar and plaster. It is added to acid soil to neutralize the acid present.

**Mortar and plaster.** Ordinary mortar is a mixture of calcium hydroxide and sand. When it is exposed to the air or spread upon porous materials, moisture is removed from it (partly by absorption into the porous materials and partly by evaporation) and the mortar becomes firm, or sets. At the same time carbon dioxide is slowly absorbed from the air, and hard calcium carbonate is formed:



By this combined action the mortar becomes very hard and adheres firmly to the surface upon which it is spread. The sand serves to give body to the mortar and makes it porous; it also prevents too much shrinkage. Plaster is a mixture of calcium hydroxide and hair or wood fiber, the latter serving to hold the mass together.

**Bleaching powder.** We have seen that when chlorine is passed into a cold solution of potassium hydroxide a mixture of potassium chloride and potassium hypochlorite is formed (p. 442). In a similar way, when chlorine is passed into a cold solution of calcium hydroxide, a mixture of calcium chloride and calcium hypochlorite ( $\text{Ca(ClO}_2)_2$ ) is formed. If, instead of passing the chlorine into a *solution* of calcium hydroxide, it is passed over the *solid* compound, the reaction goes in a different way and forms a white, solid compound having the formula  $\text{CaOCl}_2$  and known as *bleaching powder*, *chloride of lime*, or simply *bleach*:



Bleaching powder is prepared in large quantities for use as a bleaching agent and as a disinfectant. The commercial product contains about 35 per cent of available chlorine.



**Commercial preparation.** In the commercial preparation of bleaching powder the calcium hydroxide is spread to a depth of 2 or 3 inches upon the floor of a room, usually made of lead or concrete (Fig. 194). The chlorine, generated by the electrolysis of sodium chloride, enters near the top at *A*. Any unabsorbed chlorine passes out at *B* and into the adjoining chamber at *C*.

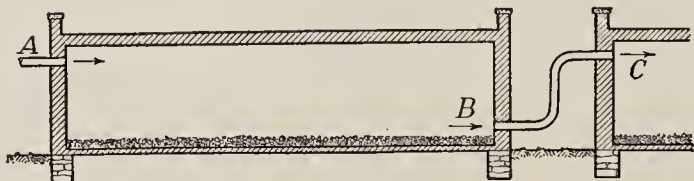
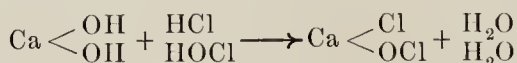
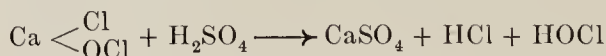


FIG 194. Diagram of a plant for the manufacture of bleaching powder

**Constitution of bleaching powder.** Bleaching powder is thought to have the structural formula  $\text{Ca} \begin{smallmatrix} \text{Cl} \\ \text{OCl} \end{smallmatrix}$ ; in other words, it is a salt of both hydrochloric and hypochlorous acid, being formed by displacing a hydrogen atom in a molecule of each of these acids by the bivalent calcium atom, thus:



Accordingly, if the compound is treated with sulfuric acid, we should expect hydrochloric acid and hypochlorous acids to be formed (p. 312), and this is what actually happens:



The two acids formed, however, at once react with each other and liberate chlorine:



If, on the other hand, bleaching powder is acted upon by a very weak acid, such as carbonic acid, only the weak hypochlorous acid is liberated:



This is the reaction which takes place when bleaching powder is exposed to the air. The hypochlorous acid liberated is an excellent bleaching and disinfecting agent.

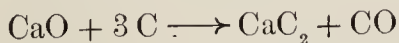
**Calcium sulfate ( $\text{CaSO}_4$ ).** Calcium sulfate occurs in nature in several different forms, the most common of which is *gypsum* ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). Over 5,000,000 tons of this mineral is quarried annually in the United States. New York, Iowa, Michigan, and Ohio produce the largest amounts. It is used as a filler in making paper (p. 400), as a constituent of fertilizers, and especially in making plaster of Paris.

Calcium sulfate is but slightly soluble in water and is precipitated in the form of a fine, white powder when concentrated solutions of a calcium salt and some sulfate are mixed together.

**Plaster of Paris ( $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$ ).** This is a fine, white powder obtained by carefully heating gypsum. When water is added to the powder, a plastic mass is formed which quickly hardens, or *sets*. This property makes it valuable for molding casts, for stucco work, and for a finishing coat on plastered walls. Broken bones are often held in place by casts of plaster of Paris until they grow together. When mixed with paper pulp and allowed to set in the form of boards, it forms a material much used in the construction of buildings, especially in place of plaster.

In the manufacture of plaster of Paris the temperature must not be allowed to rise much above  $125^\circ$ ; otherwise the anhydrous salt is formed, and this combines with water so slowly as to render it worthless for the purposes for which plaster of Paris is used.

**Calcium carbide ( $\text{CaC}_2$ ).** This compound is prepared on a large scale for use in the manufacture of acetylene (p. 371) and in making fertilizers. It is made by heating a mixture of lime and coke in an electric furnace:



The pure carbide is a colorless, transparent solid. The commercial article is a dull-gray, porous substance which contains many impurities. It is placed on the market in air-tight containers.

**Commercial preparation.** Calcium carbide was first prepared in 1836. It did not become a commercial product until 1893, when the Canadian engineer Willson found a cheap method for its

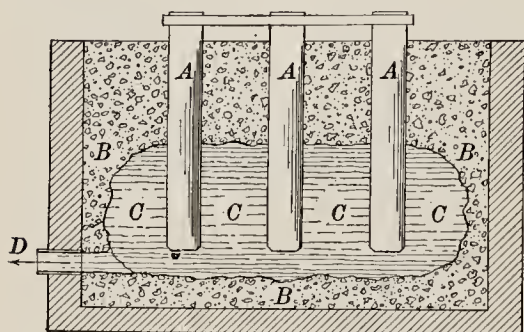
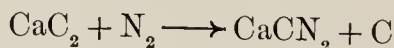


FIG. 195. Cross section of a furnace for the manufacture of calcium carbide

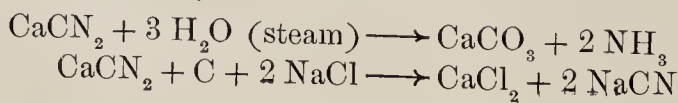
preparation. The general principles involved in its preparation are illustrated in Fig. 195. A large brick compartment open at the top is fitted with carbon electrodes *A, A, A*, and filled with a mixture *B* of lime and coke. Sufficient current is used to secure a temperature of about  $2000^{\circ}$ . The carbide forms in accordance with the above equation. It melts as fast as it forms, and the molten carbide *C, C* is drawn off from time to time through the opening *D*.

**Calcium cyanamide ( $\text{CaCN}_2$ ).** When nitrogen is passed over hot calcium carbide (Fig. 196) the two react, forming a compound known as calcium cyanamide:



The commercial product is impure, containing about 60 per cent of the calcium cyanamide; the impurities are chiefly lime and carbon. This is ground, mixed with water (which slakes the lime present), and in this form sold as a fertilizer under the name of *cyanamide*. Its value as a fertilizer lies in the fact that all its nitrogen is available as a plant food.

Calcium cyanamide promises also to become of importance in the commercial preparation of ammonia and sodium cyanide, both of which can readily be obtained from it in a manner indicated by the following equations:



The nitrogen used in the preparation of the cyanamide is obtained from liquid air (p. 89). By means of the above reactions it is possible, therefore, to convert the nitrogen of the air into important compounds of nitrogen. In the plant built at Muscle Shoals, Alabama, during the World War calcium cyanamide was made and ammonia obtained from this by the action of steam in accordance with the above equation.

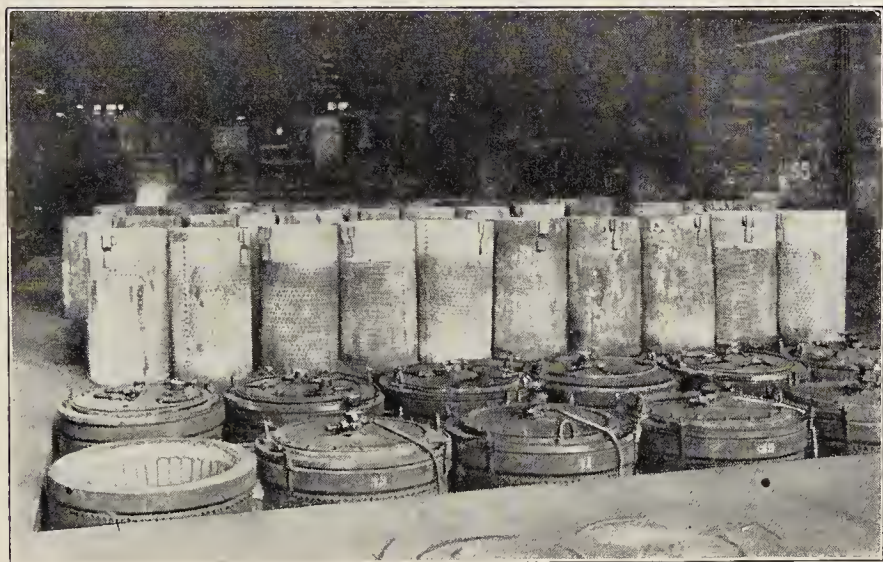


FIG. 196. View in a plant for the manufacture of calcium cyanamide

Calcium carbide is placed in the perforated steel cans shown in the background. These are then lowered into the furnaces shown in the foreground. The carbide is heated to about  $1000^{\circ}$ , and then pure nitrogen obtained from liquid air is passed over it, the two reacting to form a mixture of calcium cyanamide and carbon

**Phosphates of calcium.** With phosphoric acid, calcium forms three salts, the names and formulas of which are as follows:

Normal calcium phosphate . . . . .	$\text{Ca}_3(\text{PO}_4)_2$
Calcium monohydrogen phosphate . . . . .	$\text{CaHPO}_4$
Calcium dihydrogen phosphate . . . . .	$\text{Ca}(\text{H}_2\text{PO}_4)_2$

The normal phosphate, usually called simply calcium phosphate, is found in quantities in nature, largely in the form of rock phosphate or *phosphorite* and as a constituent of the



mineral *apatite*. It is the chief mineral constituent of bones, the ash of which contains about 80 per cent of this compound. The phosphates are of great importance in connection with the subject of fertilizers (see page 325 and end of this chapter).

**Other compounds of calcium.** *Calcium chloride* ( $\text{CaCl}_2$ ) occurs in sea water and is formed in large quantities as a by-product in the Solvay process for making sodium carbonate. The anhydrous salt readily absorbs moisture and is used as an agent for drying gases. Large quantities of calcium chloride are used (1) for laying the dust on roads (and tennis courts), (2) for making the brine used in the manufacture of artificial ice (p. 127), and (3) as a constituent of cement. *Calcium fluoride* ( $\text{CaF}_2$ ) occurs in nature in the form of *fluorite*. It is mined in large quantities, especially in Illinois and Kentucky, and is used in the preparation of hydrofluoric acid, in the manufacture of opaque glass, and in various metallurgical operations. *Calcium sulfide* ( $\text{CaS}$ ) is a by-product in the Leblanc process for making sodium carbonate. The commercial salt is sometimes used as a luminous paint, since, after exposure to a bright light, it will glow in the dark. The sulfides  $\text{CaS}_4$  and  $\text{CaS}_5$  are used as an insecticide (p. 279). *Calcium acid sulfite* ( $\text{Ca}(\text{HSO}_3)_2$ ) is used as a preservative, and in large quantities in the manufacture of paper (p. 400). A number of *calcium silicates* are known and derive their chief interest from the fact that they are important constituents of cement and glass.

## STRONTIUM AND BARIUM

**General.** These elements themselves are much rarer than calcium, are difficult to prepare, and have no commercial uses. Their most abundant minerals are the following:

Celestite . . . . .	$\text{SrSO}_4$	Barite . . . . .	$\text{BaSO}_4$
Strontianite . . . . .	$\text{SrCO}_3$	Witherite . . . . .	$\text{BaCO}_3$

Volatile compounds of strontium and of barium color the Bunsen flame, strontium imparting a red color and barium a green color. The compounds of barium and strontium are similar in composition and properties to the corresponding compounds of calcium. The important ones are described below.

**Strontium nitrate** ( $\text{Sr}(\text{NO}_3)_2$ ). This compound imparts a crimson color to flames and is used in the manufacture of fireworks and signal lights.

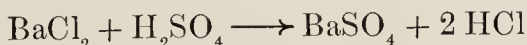
**Oxides of barium; barium hydroxide.** Barium oxide ( $\text{BaO}$ ) can be obtained by strongly heating the nitrate:



When heated to a low red heat in the air the oxide combines with oxygen, forming the peroxide  $\text{BaO}_2$ , which is used in making hydrogen peroxide (p. 82). Barium oxide readily combines with water to form the hydroxide  $\text{Ba}(\text{OH})_2$ , a white solid which is more soluble in water than calcium hydroxide.

**Barium chloride** ( $\text{BaCl}_2$ ). Barium chloride is a white solid, and from its solution it crystallizes as the hydrate  $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$ . It is used in the laboratory as a reagent to detect the presence of sulfuric acid or soluble sulfates, since it reacts with these to form the insoluble barium sulfate.

**Barium sulfate** (barite) ( $\text{BaSO}_4$ ). Barium sulfate occurs in nature as a heavy white mineral known as *barite* or *barytes*. It is precipitated as a crystalline powder when a barium salt is added to a solution of a sulfate or to sulfuric acid:



It is used in large quantities in the manufacture of paint.

**Barium nitrate** ( $\text{Ba}(\text{NO}_3)_2$ ). This compound is an oxidizing agent. When ignited with some oxidizable substance it gives a brilliant green light and is used for this purpose in the manufacture of fireworks.

## FERTILIZERS

**Plant food; fertilizers.** With the exception of carbon dioxide (and possibly a little oxygen) absorbed from the air, the growing plant derives its nourishment from the soil. In order that vegetation may thrive it is essential, therefore, that the soil should contain an adequate supply of appropriate plant food. Moreover, since this supply is continually being drawn upon by the growing

plant, it is necessary, in order that the soil may retain its fertility, that the ingredients so withdrawn shall be returned to it. It is for this purpose that fertilizers are used.

**Constituents of fertilizers.** While a number of elements are essential to the growth of the plant, experience has shown that in general the fertility of the soil may be maintained by adding four substances: (1) nitrogenous matter, (2) phosphates of calcium, (3) compounds of potassium, and (4) compounds of sulfur. It should be added, however, that our knowledge concerning the growing plant, especially as to what substances are essential to its growth, is far from complete. This subject is an attractive and important one for study and investigation. The Federal government and the various states spend large sums of money annually in maintaining the experiment stations where experiments are conducted with fertilizers, as well as with problems of all kinds that have to do with the agricultural industry.

**Sources of fertilizers.** The commercial sources of each of the constituents of fertilizers are as follows:

1. **Nitrogenous matter.** This is obtained from a number of sources: sodium nitrate, ammonium sulfate, and cyanamide; also nitrogenous organic matter, such as dried blood, the waste from slaughterhouses, and, especially, animal excrements.

2. **Phosphates.** Ground bones are especially valuable, since they contain some nitrogen in addition to calcium phosphate. This source, however, is entirely inadequate, and the great supply comes from the rock phosphates, which contain about 70 per cent of calcium phosphate. These rock phosphates are quarried in large quantities, especially in Florida (Fig. 128) and Tennessee. Since calcium phosphate is nearly insoluble, the rock is ground and then treated with sulfuric acid. This converts the insoluble calcium phosphate into a soluble calcium acid phosphate (p. 325). The resulting mixture of calcium sulfate and calcium acid phosphate is a powder known as *superphosphate of lime* and is a valuable fertilizer. Certain products (slags) formed in the manufacture of steel contain phosphorus and are used in fertilizers.

3. **Potassium compounds.** These are obtained chiefly from the Stassfurt mines (p. 440) and from Alsace, France.

4. **Sulfur compounds.** In the discussion of phosphates, under 2, it was pointed out that the ordinary *superphosphate of lime* contains calcium sulfate as a constituent. It was formerly thought

that the efficiency of the superphosphate depended entirely on the phosphorus present; it is now known that the calcium sulfate is also useful. Experiments are being conducted with a view to finding out something more definite in regard to the part that sulfur plays in the growth of the plant.

**Commercial fertilizers.** Commercial fertilizers are, as a rule, mixtures of two or more of the fundamental materials mentioned above. The composition of the fertilizer is varied according to the crop to be grown and also according to the nature of the soil upon which the fertilizer is to be used. For example, potatoes thrive best in a soil rich in potassium compounds, while wheat is benefited more by phosphates.

**Liming soils.** Sometimes a soil becomes sour, or acid, owing to the formation of acids which are often derived from decomposing vegetable matter. Certain plants, such as mosses and huckleberries, will thrive in acid soil, but grass, clover, and grain crops will not. In such cases the soil must be *sweetened* by spreading calcium hydroxide (slaked lime) upon it to neutralize the acids present, the process being called *liming* the soil. An acid soil may be detected by moistening strips of blue litmus and covering them for a few minutes with the moist soil.

**Utilization of atmospheric nitrogen.** It has been pointed out that with few exceptions plants have not the power of assimilating free nitrogen (p. 90). Moreover, it is inevitable that the supplies of sodium nitrate and ammonium sulfate, which are now the chief nitrogenous products used in the manufacture of commercial fertilizers, will sooner or later become exhausted. It has been found possible to utilize the inexhaustible supply of nitrogen in the atmosphere by converting the nitrogen into compounds which contain the element in a form available for plant food. We have already discussed some of these methods. Thus, the nitrogen may be combined with hydrogen (p. 220) to form ammonia from which ammonium sulfate may be made; or nitrogen may be passed over hot calcium carbide to form calcium cyanamide (p. 470). All the methods used for this purpose will be brought together in a later chapter.



## EXERCISES

1. What properties have the alkaline earth metals in common with the alkali metals? In what respect do they differ?
2. Write the equation for the reaction between calcium carbide and water.
3. Why does an air draft maintained in a limekiln increase the speed of the decomposition of the limestone?
4. Would air-slaked lime do for making mortar? Would it serve for liming acid soils?
5. Why should you expect calcium carbide to contain impurities?
6. How do you explain the fact that calcium carbonate can be decomposed into calcium oxide and carbon dioxide, and yet calcium oxide absorbs carbon dioxide from the air to form the carbonate?
7. Could barium hydroxide be used in place of calcium hydroxide in testing for carbon dioxide?
8. Calcite and gypsum often resemble each other in appearance. How could you easily distinguish between the two?
9. Suggest a method for preparing ammonium nitrate, starting with calcium cyanamide.
10. Calcium acid sulfite is prepared from calcium hydroxide in a manner perfectly analogous to the preparation of the acid carbonate. Write the equation for the reactions involved.
11. How could you prepare calcium chloride from calcium sulfate? barium chloride from barite?
12. How could you prove that dried mortar contains calcium carbonate and sand?
13. Starting with limestone and sulfur, how could you prepare the calcium acid sulfite used in the manufacture of paper?
14. Write the equation for the reaction that you would expect to take place when bleaching powder is treated with hydrochloric acid.
15. Suppose you wished to manufacture bleaching powder. (a) What raw materials would be required? (b) What by-products would be formed?
16. Starting with marble (pure  $\text{CaCO}_3$ ), prepare a chart (similar to the one for sodium compounds, p. 438), showing how the important compounds of calcium can be prepared either directly or indirectly from marble.

17. (a) If bleaching powder is pure  $\text{CaOCl}_2$ , what per cent of chlorine does it contain? (b) How does this compare with the percentage of chlorine in the commercial bleaching powder?

18. What weight of plaster of Paris can be made by heating 1 ton of gypsum?

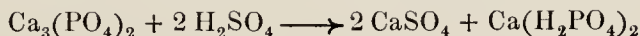
19. What weight of limestone is necessary to prepare 10 tons of lime?

20. What weight of water is necessary to slake 1 ton of lime?

21. Calculate the weight of calcium oxide present in the lime made by heating 1 ton of limestone containing 90 per cent of calcium carbonate. What weight of water would be required to slake the resulting calcium oxide?

22. The heat evolved in the slaking of 100 kg. of lime would raise the temperature of what weight of water from room temperature (say  $18^\circ$ ) to boiling?

23. In the manufacture of fertilizer what weight of sulfuric acid containing 50 per cent by weight of hydrogen sulfate would be necessary for the treatment of 1 ton of phosphate rock, on the supposition that the only reaction taking place is expressed by the following equation:



## CHAPTER XXXV

### THE MAGNESIUM FAMILY

	ATOMIC WEIGHT	DENSITY	MELTING POINT	BOILING POINT	OXIDE
Beryllium (Be) ✓ . . .	9.02	1.80	1350°(?)		BeO
Magnesium (Mg) . . .	24.32	1.74	651.0°	1110°	MgO
Zinc (Zn) . . . . .	65.38	7.14	419.4°	907°	ZnO
Cadmium (Cd) ✓ . . .	112.41	8.64	320.9°	767°	CdO

**The family.** In the magnesium family are included the five elements, beryllium, magnesium, zinc, cadmium, and mercury. Among the first four of these metals there is a close family resemblance, such as has been traced between the members of the two preceding families. Mercury will be described in connection with copper, since these two metals are below hydrogen in the electrochemical sense and on this account have much in common. Each of the metals listed in the above table ordinarily acts as a bivalent element; hence, as a rule, the formulas of their compounds are similar to the formulas of the corresponding compounds of the alkaline earth metals. Beryllium (sometimes known as glucinum) is a rare metal of little importance at present, so that no further mention will be made of it.

### MAGNESIUM

**The element.** Magnesium was first isolated in 1807 by Davy, who obtained it by the method used in isolating the alkali and alkaline earth metals. It is a light, silver-white metal just heavy enough to sink in water. Air does not act rapidly upon it, but a thin film of oxide forms upon its surface, dimming

its bright luster. It slowly decomposes boiling water and combines directly with most of the nonmetals, even with nitrogen. The common acids dissolve it, with the formation of the corresponding salts. When heated in the air it is easily ignited and burns with a brilliant white light, forming the oxide, together with a small percentage of the nitride. This light is very rich in the rays which affect a photographic plate, so that the powdered metal, either alone or mixed with potassium chlorate, is used as a source of artificial light in photography, as well as in pyrotechnics. It was especially adapted for making flares used during the World War for lighting up the battlefields. It is also used in the manufacture of certain alloys, such as *magnalium*, a light alloy of magnesium and aluminum having a high tensile strength.

**Occurrence.** Magnesium is not quite so abundant as calcium (p. 22). Like calcium, it is a constituent of many rocks and also occurs in the form of soluble salts. *Dolomite* ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ) and *magnesite* ( $\text{MgCO}_3$ ) occur in large quantities. *Asbestos*, *talc*, and *serpentine* are silicates of magnesium. The element is also a constituent of *chlorophyll*, the green coloring matter of plants; and this suggests that the metal may play an important part in the growth of the plant.

**Preparation.** The metal magnesium, like most metals whose oxides are difficult to reduce with carbon, is made by electrolysis, the anhydrous chloride or the mineral carnallite (p. 440) being used as the electrolyte. The electrolyte is melted in an iron pot, which also serves as the cathode in the electrolysis, while a rod of carbon dipping into the melted salt serves as the anode. The apparatus is very similar to those employed in the preparation of sodium and calcium.

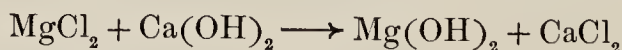
**The compounds of magnesium.** The compounds of magnesium are somewhat similar to the corresponding compounds of calcium. They can be easily prepared from the carbonate (magnesite) by the action of appropriate acids. Moreover, magnesium chloride is a constituent of *carnallite* (p. 440) and



is obtained in large quantities in the preparation of potassium chloride. The most important of the compounds of magnesium are described below.

**Magnesium oxide (magnesia) (MgO).** Magnesium oxide, sometimes called *magnesia* or *magnesia usta*, resembles lime in many respects and is prepared in the same way; namely, by heating the carbonate. It is a white powder, very soft and bulky, and is unchanged by heat even at very high temperatures. For this reason it is used in the manufacture of crucibles, in making fire brick for lining furnaces, and for other purposes where a highly refractory basic substance is needed.

**Magnesium hydroxide (Mg(OH)<sub>2</sub>).** Magnesium oxide combines with water to form the hydroxide, Mg(OH)<sub>2</sub>, but the union takes place much more slowly and with the liberation of less heat than in the case of calcium oxide (lime). Since magnesium hydroxide is but slightly soluble in water, it can be precipitated by adding a soluble base to a salt of magnesium:



It dissolves sufficiently to give a slightly alkaline reaction and is a moderately strong base.

**Magnesium carbonate (MgCO<sub>3</sub>).** Magnesium carbonate occurs in a number of localities as *magnesite*, which is usually amorphous but sometimes forms pure crystals resembling calcite. More frequently magnesium carbonate is found associated with calcium carbonate. The mineral *dolomite* has the composition CaCO<sub>3</sub> · MgCO<sub>3</sub>. Limestone containing smaller quantities of magnesium carbonate is known as *dolomitic limestone*. Dolomite is one of the most common rocks, forming whole mountain masses. It is harder and less readily attacked by acids than limestone. It is valuable as a building stone and for foundations, for lining certain types of furnaces, and as ballast for roadbeds. Magnesite is mined in California and used for making fire brick and other refractory material. The cheaper dolomite is gradually replacing it for such uses.

Like calcium carbonate, magnesium carbonate is insoluble in water but readily dissolves in water containing carbon dioxide, forming the acid carbonate :



When a solution of a magnesium salt is precipitated with sodium carbonate, a white basic carbonate is obtained, known as *magnesia alba*, which is used as a cosmetic and as a medicine.

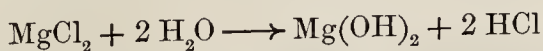
**Boiler scale.** When water which contains certain salts in solution is evaporated in steam boilers, a hard, insoluble material called *scale* deposits in the boiler. The formation of this scale may be due to several distinct causes:

1. *To the deposit of calcium sulfate.* This salt, while sparingly soluble in cold water, is almost completely insoluble in superheated water. Consequently it is precipitated when water containing it is heated in a boiler.

2. *To decomposition of acid carbonates.* As we have seen, calcium acid carbonate and magnesium acid carbonate are decomposed on heating, forming insoluble normal carbonates :



3. *To hydrolysis of magnesium salts.* Magnesium chloride and, to some extent, magnesium sulfate undergo hydrolysis when superheated in solution, and the magnesium hydroxide, being sparingly soluble, is precipitated :



The scale adheres tightly to the boiler tubes in compact layers (Fig. 197) and, being a nonconductor of heat, causes much waste



FIG. 197. Cross section of a boiler tube showing the deposit of scale

of fuel. It is very difficult to remove, owing to its hardness and its resistance to reagents. Thick scale sometimes cracks, and the water coming in contact with the overheated iron causes an explosion.

**Magnesium chloride ( $\text{MgCl}_2$ ).** This compound is found in many natural waters and salt deposits and is obtained as a by-product in the manufacture of potassium chloride from carnallite. Under ordinary conditions it crystallizes from solutions as the hexahydrate  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ , although a number of other hydrates are known. When the hydrate is heated, magnesium oxide is formed:



Owing to the abundance of magnesium chloride, attempts have been made to utilize this reaction in the preparation of both magnesium oxide and hydrochloric acid.

Magnesium also forms oxychlorides which are coming into use especially for making floors and terra cotta. A common floor covering is made by adding magnesium chloride to a mixture of fiber (wood or asbestos) and magnesium oxide. With the proper amount of water the materials set, owing to the formation of the oxychloride,  $3 \text{MgO} \cdot \text{MgCl}_2 \cdot 10 \text{H}_2\text{O}$ .

**Magnesium sulfate ( $\text{MgSO}_4$ ).** Like the chloride, magnesium sulfate is found rather abundantly in springs and in salt deposits. Deposits of the almost pure solid salt having the composition  $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$  have been found in Wyoming and Washington. It is often called *Epsom salt* because of its occurrence in the waters of the Epsom springs in England.

Magnesium sulfate is used to a slight extent in the preparation of sodium and potassium sulfates, for weighting cotton cloth in the dye industry, in tanning, and in the manufacture of paints and laundry soaps. To some extent it is used in medicine.

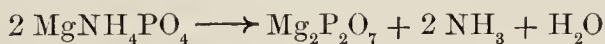
**Magnesium silicates.** Many silicates containing magnesium are known, and some of them are important substances. *Serpentine*, *asbestos*, *talc* (or *soapstone*), and *meerschaum* are examples

of such substances. *Asbestos* is soft and fibrous and a non-conductor of heat and of electricity. It is used for fireproof material in a great variety of forms, such as cloth, paper, board, and rope, and as a covering for pipes, furnaces, and boilers, to diminish heat radiation. It also has many uses as an insulator in electrical devices. The chief source of asbestos is the province of Quebec, Canada. Soapstone is valuable for sinks and table tops and, in finely ground form, as a toilet powder and foot ease. It is sometimes called *French chalk*. Meerschäum is used for pipe bowls and similar articles.

**Magnesium phosphates.** The phosphates of magnesium are similar in composition and properties to those of calcium (p. 471). When a solution of disodium phosphate is added to a solution of any magnesium compound containing ammonium hydroxide, magnesium ammonium phosphate is precipitated:



When this is filtered off and heated, it decomposes into magnesium pyrophosphate, which is a stable compound:



From the weight of the pyrophosphate it is possible to calculate the weight of magnesium present in the original solution. These reactions serve in the laboratory for the quantitative determination either of magnesium or of phosphoric acid.

## ZINC

**Preparation.** The metals so far studied are all rather difficult to prepare, so that none of them have come into any very extended use. Zinc, on the other hand, is rather easily obtained from its ores and possesses properties that make it useful for many purposes. As a result it has long been known and used. The ancients were familiar with brass, an alloy of zinc and copper, while jewelry made of zinc has been found in ruins of cities that were destroyed before the beginning of the Christian Era.



**Properties and chemical conduct.** Pure zinc is a rather heavy, bluish-white metal with a high luster. It melts at about  $420^{\circ}$ , and if heated much above this temperature in the air it takes fire and burns with a bluish flame. It boils at  $907^{\circ}$ .

Many of the properties of zinc are much influenced by the temperature and previous treatment of the metal. When cast into ingots from the liquid state it becomes at ordinary temperatures hard, brittle, and highly crystalline. At temperatures between  $100^{\circ}$  and  $150^{\circ}$  it is malleable and can be rolled into thin sheets, which retain their softness and malleability at ordinary temperatures. Above  $150^{\circ}$  it again becomes very brittle. When melted and poured slowly into water, it forms thin, brittle flakes and in this condition is called *mossy zinc*.

Zinc tarnishes superficially in moist air, owing to the formation of a basic carbonate. It does not decompose even boiling water, but at a high temperature it acts upon steam, forming the oxide and hydrogen. When heated sufficiently in oxygen or air it burns with a bluish flame. Dilute acids have but little action upon the pure metal, since the hydrogen at first liberated collects on the surface of the metal in the form of a thin film, and the action soon ceases. If another metal below zinc in the electrochemical series, such as iron, copper, or platinum, is present, either as an impurity or simply in contact with the zinc, the hydrogen escapes from the surface of the less positive metal, and the zinc rapidly dissolves. Zinc also dissolves in solutions of strong bases with liberation of hydrogen.

**Occurrence.** Zinc is not a constituent of common rocks, and its occurrence is rather local and confined to deposits or pockets. Its chief ores are the following: *sphalerite* ( $\text{ZnS}$ ); *zincite* ( $\text{ZnO}$ ); *smithsonite* ( $\text{ZnCO}_3$ ); *willemite* ( $\text{Zn}_2\text{SiO}_4$ ); *calamine* ( $\text{Zn}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$ ); *franklinite* ( $\text{ZnFe}_2\text{O}_4$ ). In the United States it occurs in a number of different localities but most abundantly in the Joplin district, which is made

up of parts of the states of Oklahoma, Kansas, and Missouri. New Jersey also produces large quantities. It is interesting to note that minute percentages of zinc are present in many forms of marine life.

**Metallurgy.** In the metallurgy of zinc the ores are first converted into the oxide by roasting, and the oxide is then reduced with carbon.

A mixture of zinc oxide and coal is heated in earthenware retorts. The zinc oxide is thereby reduced, and the resulting zinc, being volatile at the temperature of the retort, distills and is collected in suitable receivers. At first the zinc collects in the form of a powder known as *zinc dust*, which, however, contains some zinc oxide. Later, when the receiver has become hot, the zinc condenses to a liquid and is drawn off into molds. In this form it is impure and is known as *spelter*.

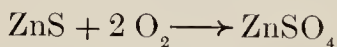
Commercial zinc ordinarily contains a number of impurities, especially carbon, arsenic, cadmium, and iron. These can be largely removed by distillation. Zinc containing less than 0.001 per cent of impurities has been obtained by electrolysis of a pure salt and subsequent distillation under diminished pressure.

**Uses of zinc.** The chief use of zinc is in the manufacture of *galvanized iron*. This is sheet iron covered with a thin layer of zinc, which protects the iron from the action of air and water. About two thirds of all the zinc produced is used in this way. Large quantities are also used in the manufacture of alloys. The metal is also used in the construction of batteries and as a roofing material. In the laboratory it is used in the preparation of hydrogen.

**Compounds of zinc.** In general the compounds of zinc are similar in formula and appearance to those of magnesium. They often differ from them quite markedly, however, in chemical conduct. Either the metal, its oxide, or the natural carbonate or sulfide serves as a convenient material for the preparation of these compounds.

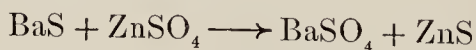
**Zinc oxide (zinc white) ( $\text{ZnO}$ ).** This is a white powder obtained by roasting the ores in a current of air or, in the pure state, by oxidizing the metal itself. It turns yellow when heated, but regains its white color on cooling. It is used very largely as a white pigment in paints, under the name of *zinc white*, and has an advantage over white lead in that it is not darkened by the sulfur compounds which are present in the air, especially in manufacturing districts. Large quantities are also used annually in the manufacture of rubber goods, especially automobile tires (p. 489).

**Zinc sulfate ( $\text{ZnSO}_4$ ).** This salt crystallizes from concentrated solutions in the form of the hydrate  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , which has long been known as *white vitriol*. It is prepared commercially by the careful roasting of the sulfide:



Zinc sulfate is used to a limited extent as a medicine and in the dyeing and printing of cloth.

**Zinc sulfide ( $\text{ZnS}$ ).** This substance occurs as the mineral *sphalerite* and is one of the most valued ores of zinc. Very large deposits occur in southwestern Missouri. The natural mineral is found in large crystals or masses resembling rosin in color and luster. It is insoluble in water and when prepared by precipitation is white. *Lithopone* is a mixture of the two solids barium sulfate and zinc sulfide. It is a valuable material for making white paint, and large quantities of it are prepared for this purpose by bringing together barium sulfide and zinc sulfate in solution:



**Zinc chloride ( $\text{ZnCl}_2$ ).** This salt is very soluble in water and has a strongly acid reaction. It has germicidal properties and is used as a wood preservative, especially for railroad ties.

**Preservation of wood.** With the rapid disappearance of the forests the preservation of wood from decay (fungous growths) becomes a very important problem. When the wood is to be

exposed merely to atmospheric conditions it is preserved by paints and varnishes. When it must be partly buried in the ground (railway ties, fence posts) it is treated with germicidal preservatives. Those most frequently used are zinc chloride and coal-tar creosote.

The wood is placed in closed boilers in baths of the appropriate liquid, and the air is exhausted so that the liquid may be more readily driven into the pores of the wood. Frequently the latter process is assisted by the application of considerable pressure to the liquid after the air has been pumped out.

### CADMIUM

**The element.** This element occurs in small quantities in some zinc ores, being present in the ratio of 1 part of cadmium to about 200 parts of zinc. In the course of the metallurgy of zinc the cadmium compounds undergo chemical changes quite similar to those of the zinc compounds, and the cadmium distills along with the zinc. Being more volatile, it comes over with the first of the zinc and is prepared from the first portions of the distillate by special methods of purification. The element very closely resembles zinc in most respects. Some of its alloys (see Wood's metal, p. 336) are characterized by having low melting points. The United States and Germany are the only cadmium-producing countries. The metal is used chiefly in making low-melting alloys for automatic fire sprinklers (p. 336) and safety plugs for steam boilers. Small quantities are also used for dental alloys and electric fuses. For scientific purposes, it is of great value as a material for the cathode in a standard cell.

**Compounds of cadmium.** Among the compounds of cadmium may be mentioned the chloride,  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ , the sulfate,  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ , and the nitrate,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . These are white solids soluble in water. The sulfide,  $\text{CdS}$ , is a bright-yellow substance which is insoluble in water and in dilute acids. It is a valuable pigment in fine paints.



## RUBBER

**Production.** The statement has been made (pp. 138, 486) that large quantities of carbon black and zinc oxide are used in making certain rubber goods, and this suggests a brief discussion of rubber itself, since it has become such an important article in



FIG. 198. View on a rubber plantation; tapping the tree

our modern life. Over 600,000,000 lb. of rubber is used annually in the United States, about 75 per cent of which goes into the motor-car industry.

Rubber is the product of a rubber tree (of which there are many species) which grows wild in the upper Amazon region of South America and is cultivated in large numbers in tropical regions (Fig. 198) such as Java, Sumatra, Ceylon, and the Malay States. The percentage of rubber obtained from cultivated trees has increased very rapidly as the demand for rubber has increased.

In 1900 only a very small fraction of 1 per cent was obtained from this source, while at present over 75 per cent of the world's output of rubber comes from the rubber plantations. The rubber is obtained from the trees by tapping (cutting through the bark), as shown in Fig. 198. The sap runs from the incisions down the trees and is collected in buckets. This sap, which is known as the *latex*, is really an emulsion consisting mainly of minute rubber particles dispersed in water. It resembles milk in appearance and is similar to it in that the rubber particles are dispersed in it much as the fat is

dispersed in fresh milk; but while milk contains from 3 to 5 per cent of fat, the latex contains from 25 to 35 per cent of rubber. Geer, in his fascinating book on "The Reign of Rubber," states that the number of these particles is so great that if those present in one gallon of latex were placed side by side they would make a tiny rubber thread 372 miles long. The latex contains a small amount of nitrogenous matter which acts as a protective colloid (p. 357), thus preventing the separation of the rubber particles. In order to separate the rubber a little acetic acid is added. This acts upon the protective colloid so that it no longer functions in that capacity, and the rubber at once separates in the form of a soft, white dough. This is then washed and pressed so as to remove all foreign matter, and in this form is known as *raw rubber*.

**Composition.** Pure rubber is a hydrocarbon whose molecular formula is some multiple of the simple formula  $C_5H_8$ ; hence the formula is generally written  $(C_5H_8)_x$ . Rubber can be made in the laboratory, but the process, as yet developed, is so costly that the synthetic rubber cannot compete with the natural product. Nevertheless, during the World War the Germans, shut off from natural supplies, made a considerable quantity of rubber and even equipped a few automobiles with tires made of the synthetic product.

**Vulcanizing rubber.** The raw rubber is so readily affected by the temperature that it is worthless for most purposes. An article made of it would become hard and brittle in the winter and would melt in the summer. In 1839 Charles Goodyear of New Haven, Connecticut, found that if rubber is heated with a small percentage of sulfur under proper conditions, these objectionable qualities are removed. This process is known as *vulcanization*. It is not known with certainty just how the sulfur acts in bringing about this change.

**Rubber mixtures.** The rubber that is used in making the many "rubber" articles with which we are familiar, such as a rubber boot or a rubber tire, is not composed simply of rubber and sulfur. Investigations have shown that certain raw materials known as *pigments*, mixed with the rubber along with the sulfur, impart to the product increased strength or some other desired property. The most common of these are perhaps zinc oxide and carbon-black. The color of the article is often due to the pigment used. Thus, the red color of certain tires is due to sulfide of antimony, while the black color of other tires is due to carbonblack.

## EXERCISES

1. What properties have the metals of the magnesium family in common with the alkali metals? with the alkaline earth metals?
2. Compare the action of the metals of the magnesium group on water with that of the other metals studied.
3. What metals already studied are prepared by electrolysis?
4. Write the equation representing the reaction between magnesium and hydrochloric acid; between magnesium and dilute sulfuric acid.
5. Give the composition of commercial lime prepared from dolomite.
6. With phosphoric acid magnesium forms salts similar to those of calcium. Write the names and formulas of the magnesium salts which one might expect to be thus formed.
7. How could you distinguish between magnesium chloride and magnesium sulfate? between Glauber's salt and Epsom salt?
8. Account for the fact that paints made of zinc oxide are not colored by hydrogen sulfide.
9. Write equations showing how the following compounds of zinc may be obtained from metallic zinc: the oxide, chloride, nitrate, carbonate, sulfate, sulfide, hydroxide.
10. How could you prepare the pigment cadmium sulfide, starting with cadmium?
11. Note the position of the alkali metals, the calcium family, and the magnesium family in the electrochemical series. How should you expect acids to act upon these metals?
12. Why are none of the metals so far studied found free in nature?
13. What reaction should you expect to take place if a piece of zinc is immersed in a solution of copper sulfate? Explain.
14. What weight of carnallite is necessary for the preparation of 500 g. of magnesium?
15. What weight of franklinite is necessary for the preparation of 1 ton of zinc white?
16. 1 g. of a zinc ore was dissolved in acid and the zinc present precipitated by hydrogen sulfide. The resulting zinc sulfide weighed 0.38 g. Calculate the percentage of zinc in the ore.
17. Which would yield the more zinc, 1 ton of sphalerite or 1 ton of franklinite?

## CHAPTER XXXVI

### ALUMINUM AND THE TERVALENT METALS

**The group.** With the exception of aluminum and boron (which has already been considered) none of the elements in Group III of the periodic table are well known or abundant. One family in the group includes aluminum, together with the very rare metals *gallium* and *indium*, and the somewhat more abundant metal *thallium*; the other family includes *scandium*, *yttrium*, and *lanthanum*.

All the elements of the group are trivalent metals, though some of them, particularly thallium, have lower valences as well. With few exceptions their salts are colorless, save when they are derived from a colored acid. The bases which these metals form are nearly all weak, and many of their salts are hydrolyzed in solution. Aluminum is the only one of these metals that need be further described in this text.

**The rare earths.** Lanthanum and the fourteen elements following it (of atomic numbers 58 to 71 inclusive) constitute a very interesting and puzzling group known collectively as the *rare earths*. Instead of showing a decided change of properties as their atomic weights increase (as all other elements do), these fifteen elements are all so nearly alike in chemical properties that it has been exceedingly difficult to separate them. They are all trivalent, form very well characterized salts, and are without doubt perfectly distinct elements; yet they have no logical place in the periodic classification. They are nearly always found together in nature, and many minerals are known that contain them in very considerable quantities. Very large quantities of a mixture of all of them accumulate in the extraction of thorium from monazite sand (p. 387). The only one whose compounds are obtained in pure form rather easily is *cerium*. Compounds of cerium are used as mordants, as



catalytic agents, and in medicine and photography. An alloy of cerium with iron is used as a gas-lighter or cigar-lighter, since it gives off a stream of sparks when scratched by hard iron. Mixed salts of the other rare earths have been used as antiseptics, as mordants, and as pigments.

## ALUMINUM

**Introduction.** Aluminum is of great interest to us for many reasons. In the first place, the metal possesses a number of desirable properties, for it is fairly strong and yet it is only about one third as heavy as iron. Moreover, it has a pleasing appearance, resembling tin, and it is not acted upon to any extent by the air. These properties make it a very valuable metal for many purposes which require lightness, strength, and durability, such as the manufacture of automobiles and aëroplanes. Again, it is an interesting fact that aluminum is the most abundant of all metals (p. 22), being almost twice as abundant as iron; yet it is much more expensive than iron. The higher cost of aluminum is obviously due to the fact that it is more difficult than iron to separate from its ores, and this suggests the interesting problem of finding some way to reduce this cost and make the metal more available. Great improvements, indeed, have been made, in comparatively recent times, in the metallurgy of aluminum. For example, in 1883 only 83 lb. of the metal was produced, and the cost of the metal was about \$5 per pound. In 1918, owing to the extended uses of the metal for war purposes, the production in the United States reached a maximum amounting to 225,000,000 lb., and the price of the metal was about 30 cents per pound. Since 1918 the production has fallen off somewhat, and the price has been as low as 20 cents per pound. The United States produces about half of the world's output.

**Occurrence.** Aluminum is the most abundant of all the metals and, next to oxygen and silicon, the most abundant of all the elements. The free element is not found in nature,

but its compounds, especially the silicates, are abundant and widely distributed, being essential constituents of all important soils and rocks excepting limestone and sandstone. The *feldspars*, which are the most abundant of all the minerals in the earth's crust, are all silicates of aluminum and either sodium, potassium, or calcium. Since the soil has been formed largely by the disintegration of these rocks, it is rich in the silicates of aluminum, chiefly in the form of clay. Some of the other forms in which aluminum occurs in nature are the following: *corundum* ( $\text{Al}_2\text{O}_3$ ); *emery* ( $\text{Al}_2\text{O}_3$  colored black with oxide of iron); *cryolite* ( $\text{Na}_3\text{AlF}_6$ ); *bauxite*, a mixture of iron oxide and hydrated aluminum oxides ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ). Bauxite is the ore from which aluminum is prepared. Nearly all the bauxite used in the United States for the production of aluminum comes from Arkansas and from South America.

**Preparation.** Aluminum was first prepared by the chemist Wöhler in 1827 by heating anhydrous aluminum chloride with potassium:

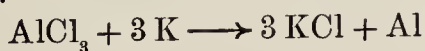


FIG. 199. Charles Martin Hall  
(1863-1914)

View of an aluminum statue of Hall, in the  
Carnegie Museum, Pittsburgh

Although the metal is very abundant in nature and possesses many desirable properties, the cost of separating it from its ores by the earlier methods was so great that it remained almost a curiosity until comparatively recent years. It is now prepared by the electrolysis of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) dissolved in a bath of molten cryolite and fluorite, — a method first patented by the American chemist Hall (Fig. 199) in 1886. The aluminum oxide used is obtained from bauxite.

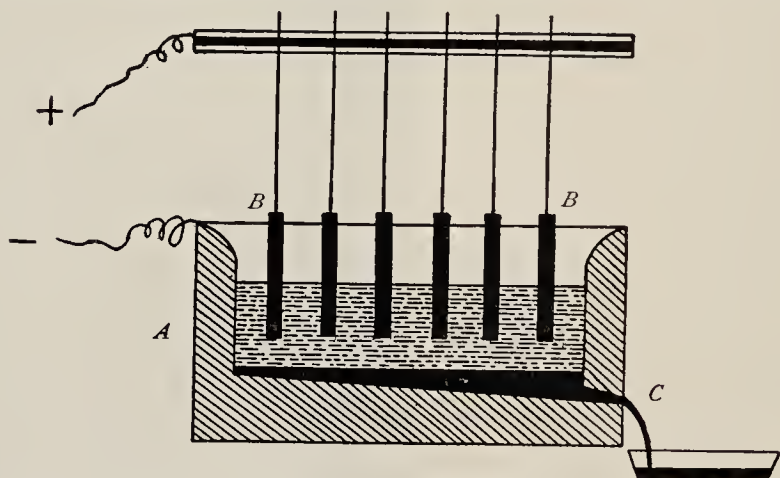


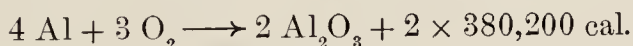
FIG. 200. Cross section of a furnace for the electrolysis of aluminum oxide

**Metallurgy.** An iron box *A* (Fig. 200) about 8 ft. long and 6 ft. wide is connected with a powerful electrical generator in such a way as to serve as the cathode upon which the aluminum is deposited. Three or four rows of carbon rods *B, B* dip into the box and serve as the anodes. The box is partly filled with cryolite and the current is turned on, generating enough heat to melt the cryolite. Aluminum oxide is then added and acts as an electrolyte, being decomposed into aluminum and oxygen. The temperature is maintained above the melting point of aluminum, and the liquid metal, being heavier than cryolite, collects on the bottom of the vessel and is tapped off from time to time through the tap hole *C*.

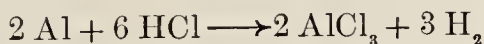
**Properties and chemical conduct.** Aluminum resembles tin in appearance. Its density is 2.65, being only about one third that of iron. It melts at  $660^{\circ}$ . It is ductile and malleable,

especially at temperatures between  $100^{\circ}$  and  $150^{\circ}$ , when it can be hammered into very thin sheets. At higher temperatures, near its melting point, it is very brittle. It is fairly hard and strong, being superior to most metals in these respects, although not equal to steel. It is an excellent conductor of heat and electricity.

Aluminum is but slightly acted upon by water, while moist air merely dims its luster. Further action is prevented in each case by the formation of a very thin film of oxide upon the surface of the metal. It combines with many of the nonmetals, especially with the halogens and the members of the sulfur family. It is an excellent reducing agent, combining with oxygen at high temperatures, with liberation of much heat:



Nitric acid and dilute sulfuric acid have but little action upon it; concentrated sulfuric acid dissolves it, forming the sulfate and liberating sulfur dioxide. Hydrochloric acid is its best solvent:



Aluminum resembles zinc in that it readily dissolves in strong alkalis, liberating hydrogen. It is also acted upon by sodium chloride, especially in the presence of oxygen and dilute acids such as acetic acid.

**Uses.** The lightness and strength of aluminum, together with its inactivity toward air and water, suggest a variety of applications for the metal. About one third of the output of the metal is used in the automobile industry. In pure form it is used for certain construction purposes and for the manufacture of cooking utensils. In the form of a fine powder suspended in a suitable liquid it makes an efficient silverlike paint. Although not as good a conductor of electricity as copper for a given cross section of wire, nevertheless, weight for weight, it is an even better conductor and is used in electrical construction, especially for long-distance power wires.



The pure metal is also used as a reducing agent in separating certain metals from their oxides and in the welding of iron (Goldschmidt process). It is used as a *deoxidizing agent* in the manufacture of iron and steel, since a small quantity added to molten steel combines with any oxygen remaining in the metal. A large number of alloys of aluminum have been prepared, and many of them are of the greatest importance. Its alloys with copper (aluminum bronze) as well as with copper and zinc are easily cast into form and are not acted upon by the air. *Duralumin* contains about 95 per cent aluminum and small amounts of copper, magnesium, and manganese. *Magnalium* (p. 479) is silver-white and very light in weight.

**Goldschmidt reduction process.** Aluminum is frequently employed as a powerful reducing agent, many metallic oxides which resist reduction by carbon being readily reduced by it. The aluminum, in the form of a fine powder, is mixed with the metallic oxide, together with some substance such as fluoride to act as a flux. The mixture is ignited, and the aluminum unites with the oxygen of the metallic oxide, liberating the metal.

**Thermite welding process.** The property possessed by aluminum of reducing oxides with the liberation of a large amount of heat is turned into practical account in the welding of metals. The German chemist Goldschmidt was the first to use aluminum for this purpose. The welding of metals by this method may be illustrated by a single example; namely, the welding of car rails, — a process often carried out in connection with electric railways to secure good electrical connection. The ends of the rails are accurately aligned and thoroughly cleaned. A sand mold *A* (Fig. 201) is then clamped about the ends of the rails, leaving sufficient space so that the metal can flow in. The ends of the rails are heated to redness by the flame from a gasoline compressed-air torch directed into the opening in the mold. Just over the opening is placed the conical-shaped crucible *B*, which contains a mixture of iron, metallic oxides, and aluminum. When the ends of the rails have

been heated to redness by the torch, the mixture in the crucible is ignited, and after a few seconds the crucible is opened at the bottom, and the molten metal resulting from the reaction in the crucible is allowed to flow into the mold. The molten metal surrounds the ends of the rails and, as it cools, welds them firmly together. A mixture of the metallic oxides and aluminum ready for use in welding is sold under the name of *thermite*.

**Compounds of aluminum.** Aluminum is a trivalent metal, and the formulas of its compounds therefore resemble those of bismuth and antimony. Aluminum hydroxide, like antimony hydroxide, is amphoteric (p. 331). With strong bases it forms *aluminates* such as sodium aluminate ( $\text{NaAlO}_2$ ), while with acids it forms salts such as the chloride  $\text{AlCl}_3$  and the sulfate  $\text{Al}_2(\text{SO}_4)_3$ . *These salts are characterized by their great tendency to undergo hydrolysis.* Aqueous solutions of the chloride and sulfate are strongly acid in reaction, while the carbonate and sulfide are completely decomposed by water (p. 246).

**Aluminum oxide ( $\text{Al}_2\text{O}_3$ ).** The occurrence of aluminum in nature in the form of *corundum* and *emery* has been mentioned already. In transparent crystals tinted different colors by traces of other substances, often in colloidal dispersion, it forms such precious stones as the *sapphire*, *ruby*, and *oriental amethyst*. All of these are very hard, falling but little short of the diamond in this respect.

By igniting the hydroxide the pure aluminum oxide may be obtained in the form of a white amorphous powder. When heated to about  $2000^\circ$  it melts, and on cooling forms a crystalline mass resembling natural corundum. Some forms of laboratory apparatus, such as crucibles and tubes, are being made of aluminum oxide. When used for this purpose the

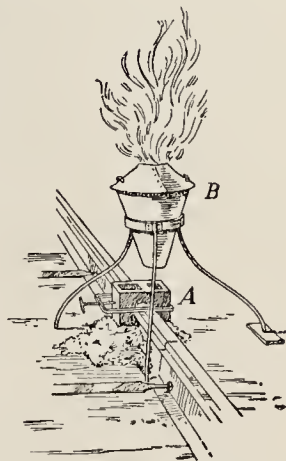
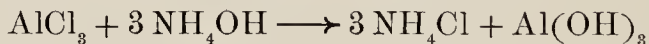


FIG. 201. Welding steel rails with thermite

oxide is known as *alundum*. Not only are the natural forms of aluminum oxide (corundum and emery) used as abrasives, but large quantities of the oxide are prepared from bauxite and sold as an abrasive under various trade names. It is especially valuable in polishing steel and iron alloys.

**Commercial preparation of gems.** A number of gems are now prepared in the laboratory from molten aluminum oxide. The white sapphires so extensively advertised are simply the pure oxide. By incorporating with the melted oxide small percentages of certain metallic oxides different tints or colors are obtained, and in this way are prepared such gems as the ruby, the oriental amethyst, and the yellow and blue sapphires, which are almost identical in composition and properties with the natural stones.

**Aluminum hydroxide ( $\text{Al}(\text{OH})_3$ ); aluminic acid ( $\text{HAlO}_2$ ).** We should expect the insoluble aluminum hydroxide to be precipitated by the action of a soluble base on a salt of aluminum:



The white, flocculent precipitate so obtained is usually given the formula  $\text{Al}(\text{OH})_3$ , but Weiser has shown that it is a typical colloidal gel consisting of the oxide in various stages of hydration. It is amphoteric in character, dissolving in acids to form aluminum salts such as  $\text{AlCl}_3$ , and in alkalis to form such salts as  $\text{NaAlO}_2$ , derived from the acid  $\text{HAlO}_2$ , or  $\text{AlO} \cdot \text{OH}$ . This acid is called *aluminic acid*, and its salts *aluminates*. Its magnesium salt,  $\text{Mg}(\text{AlO}_2)_2$ , is found in nature and is called *spinel*.

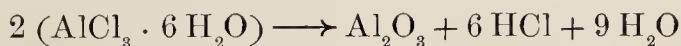
Because of its colloidal character when first formed, and also because of its ability to combine with or adsorb many coloring materials (dyes), aluminum hydroxide is a very useful reagent, both in water purification and in the dyeing industry.

**Use of aluminum hydroxide in dyeing.** Most of the dyes are prepared from compounds obtained from coal tar (hence the term *coal-tar dyes*). Many of these will not adhere to natural fibers, such as cotton; that is, they will not *dye fast*. It is often possible

to dye such cloth in the following way: The cloth is first soaked in a solution of an aluminum salt. It is then exposed to the action of steam, whereby the aluminum salt is completely hydrolyzed, the resulting aluminum hydroxide being thus thoroughly incorporated in the fiber. If the cloth is now dipped into a solution of the dye, the aluminum hydroxide combines with or adsorbs the color substance and fastens, or "fixes," it upon the fiber. A substance such as aluminum hydroxide which serves this purpose is known as a *mordant*.

The compounds which serve well as mordants may be precipitated in solutions containing various dyes, and the precipitate will be highly colored, though not always of the same color as the dye. Colored precipitates of this kind are called *lakes*.

**Aluminum chloride ( $\text{AlCl}_3$ ).** The anhydrous chloride, which is used in the synthesis of many carbon compounds, is made by heating aluminum turnings in a current of chlorine. The hydrated chloride,  $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$ , is prepared by dissolving the hydroxide in hydrochloric acid and evaporating to crystallization. When heated it is converted into the oxide, resembling magnesium chloride in this respect:

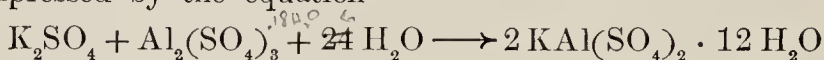


When petroleum is heated with the anhydrous aluminum chloride, under proper conditions, some of the heavier hydrocarbon molecules are broken, or "cracked" (p. 369), into lighter ones, and the yield of gasoline is thus increased. Large quantities of the chloride are used for this purpose. It is also a very valuable catalyzer in the preparation of many organic compounds.

**Aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ).** This compound is prepared by the action of sulfuric acid on bauxite. It crystallizes from water under ordinary conditions as  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ . It is cheapest of the soluble salts of aluminum and is used in the preparation of alums. Its largest use is as a source of aluminum hydroxide for the purification of water, for dyeing, and for the manufacture of certain kinds of paper.



**Alums.** Aluminum sulfate has the property of combining with the sulfates of the alkali metals to form compounds called *alums*. Thus, with potassium sulfate the reaction is expressed by the equation

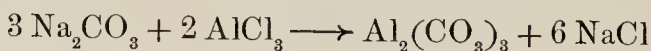


The sulfates of other trivalent metals can form similar compounds with the alkali sulfates, and these compounds are also called alums, though they contain no aluminum. They all crystallize in octahedra and contain 12 molecules of water of hydration. The alums most frequently prepared are the following:

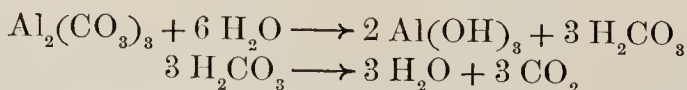
Potassium alum . . . . .	$\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$
Ammonium alum . . . . .	$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$
Ammonium iron alum . . . . .	$\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$
Potassium chrome alum . . . . .	$\text{KCr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$

Commercially the word *alum* is often used, at present, to signify aluminum sulfate.

**Hydrolysis of salts of aluminum.** While aluminum hydroxide forms fairly stable salts with strong acids, it is such a weak base that its salts with weak acids are readily hydrolyzed (p. 246). Thus, when an aluminum salt and a soluble carbonate are brought together in solution, we should expect to have aluminum carbonate precipitated according to the equation



But if it is formed at all, it instantly hydrolyzes. The products of the hydrolysis are aluminum hydroxide and carbonic acid, the latter then forming carbon dioxide and water:



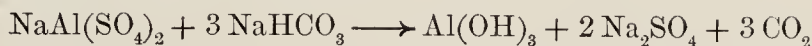
It is because of these reactions that alum is used as a constituent of some baking powders.

**Baking powders.** Every baking powder contains three ingredients, the name and function of each of which is as follows: (1) sodium bicarbonate to furnish the carbon dioxide; (2) some compound which, in the presence of water, reacts with the bicarbonate and

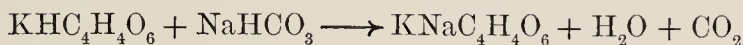
slowly liberates carbon dioxide; and (3) starch or flour, which keeps the powder dry by absorbing moisture, and hence prevents deterioration. The compounds used for liberating the carbon dioxide from the bicarbonate are either calcined sodium aluminum sulfate, cream of tartar, or calcium acid phosphate. A baking powder is generally designated by the name of the compound used to liberate the carbon dioxide. Thus, we speak of alum baking powders (meaning those containing sodium aluminum sulfate), cream of tartar baking powders, and phosphate baking powders.

The reactions taking place when water is added to each of these classes of powders are represented in the following equations:

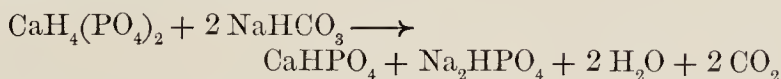
Sodium aluminum sulfate:



Cream of tartar:

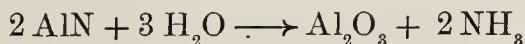


Calcium acid phosphate:



**Fire extinguishers.** The property possessed by aluminum salts of evolving carbon dioxide from carbonates is utilized also in the so-called "foamite" fire extinguishers. These consist of a receptacle which contains two separate solutions as follows: (1) A solution of sodium bicarbonate and some organic material such as an extract of licorice root, and (2) a solution of aluminum sulfate. When the receptacle is inverted (see Fig. 64 for principle involved), the two solutions come together and carbon dioxide is generated in sufficient quantities to force the liquid out of the nozzle onto the fire. The escaping carbon dioxide causes bubbles to form, and the extract of licorice makes the bubble films tough and resistant, forming over the fire a sort of blanket of bubbles filled with carbon dioxide. Such extinguishers are very effective in fighting oil fires.

**Aluminum nitride (AlN).** This compound is prepared by the direct union of aluminum and nitrogen at a high temperature. It derives its chief interest from the fact that when it is treated with steam, ammonia is formed:



The nitrogen used in preparing the nitride is obtained from the air. It is possible, therefore, through the intermediate formation of aluminum nitride, to convert the nitrogen taken from the air into ammonia.

**Aluminum silicates.** In discussing the occurrence of aluminum it was stated that the silicates of this metal are widely and abundantly distributed. Sometime in the history of the earth's formation its surface must have been composed of a solid igneous rock formed by the cooling of the molten mass. The various silicates of aluminum constitute by far the largest percentage of these igneous rocks. The most important of these are the *feldspars*, known as *orthoclase* ( $\text{KAlSi}_3\text{O}_8$ ), *albite* ( $\text{NaAlSi}_3\text{O}_8$ ), and *microcline*, which has the same chemical composition as orthoclase but is different in crystalline structure. The gradual disintegration, or weathering, of these rocks through various agencies, such as the action of air and water, has resulted in the formation of the mineral constituents of the soil. The changes taking place in the process are often very complex and are not well understood. Thus, in the weathering of orthoclase the potassium is removed, together with a portion of the silica, while at the same time water enters into chemical combination with the residue. In this way there is formed the soft, plastic mineral known as *kaolinite* ( $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , often written  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ). Large quantities of this mineral are sometimes found deposited in beds in fairly pure form. More often it has been carried away by running water and mixed with various other products resulting from the crushing and weathering of rocks, thus forming the product known as *clay*. *Kaolin* is a special kind of clay which usually burns white, so that it can be used for making chinaware. It is evident, therefore, that clay is extremely variable in composition, though the essential constituent appears to be kaolinite. *Fuller's earth* is a particular form of clay, mined in a number of states (especially in Florida) and used for clarifying both vegetable and mineral oils.

**Nitrogen fixation.** References have been made under various headings to the methods which are either being used or tested for utilizing the nitrogen of the atmosphere by converting it into useful compounds. It is desirable to bring these methods together in one place. They are as follows:

1. *The arc process* (p. 228), which results in the formation of nitric acid.

2. *The cyanamide process* (p. 470), which yields calcium cyanamide, which in turn serves for the preparation of ammonia or metallic cyanides.

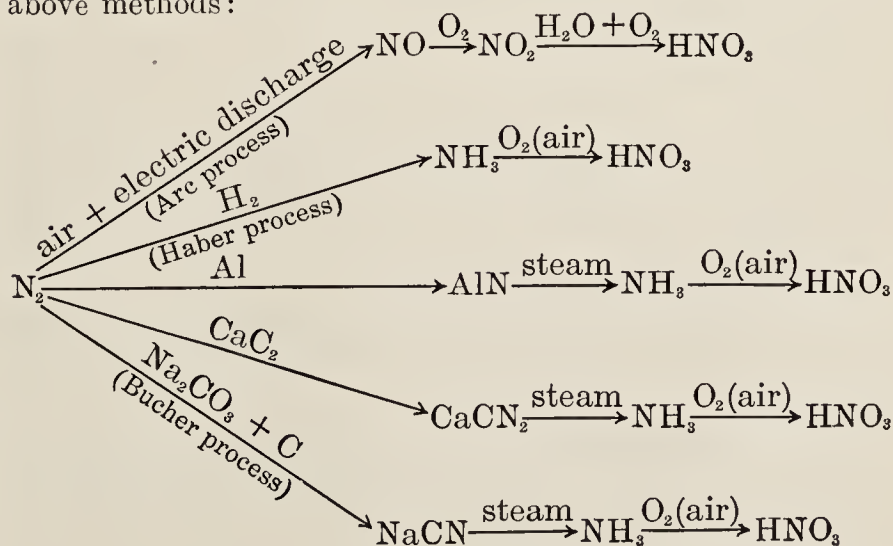
3. *The Haber process* (p. 220), which gives ammonia by direct synthesis.

4. *The Bucher process* (p. 437), which yields sodium cyanide.

5. *The nitride process* (p. 501), which consists in heating certain metals, especially aluminum, with nitrogen. Upon treating the resulting nitrides with water, ammonia is evolved.

The first three of these methods are now used commercially, and it is reasonably certain that the resulting compounds, or similar ones derived from atmospheric nitrogen, will eventually replace the sodium nitrate and ammonium salts which are now obtained from other sources and used in the manufacture of nitric acid and fertilizers.

The following diagram gives the main steps in each of the above methods:





An excellent discussion of the subject of nitrogen fixation is given in the "Report on the Fixation and Utilization of Nitrogen" prepared by the Nitrate Division, Ordnance Office, War Department, Washington, D. C.

### EXERCISES

1. What metals and compounds studied are prepared by electrolysis?
2. Write the equation for the reaction between aluminum and hydrochloric acid; between aluminum and sulfuric acid.
3. What hydroxides have we studied that have both acid and basic properties? What are such hydroxides called?
4. Write equations showing the methods used for preparing aluminum hydroxide and aluminum sulfate.
5. Write the general formula of an alum, representing an atom of a univalent metal by  $M'$  and an atom of a trivalent metal by  $M'''$ .
6. What is the significance of the term *colloid* as applied to aluminum hydroxide?
7. Compare the properties of the hydroxides of the different groups of metals so far studied.
8. In what respects does aluminum oxide differ from calcium oxide in properties?
9. Where should you expect the factories for the production of aluminum to be located?
10. Why do the directions for using aluminum cooking utensils state that such utensils must not be washed in alkaline solutions?
11. Aluminum sulfide is completely hydrolyzed by water. Write the equations for the reactions you would expect to take place when a solution of ammonium sulfide is added to a solution of aluminum chloride.
12. What is the aerating agent used in the making of bread? Why not use baking powder?
13. A mixture of sour milk and sodium bicarbonate is sometimes used as an aerating agent in place of baking powder. What is the chemistry involved? Would lemon juice serve the same purpose as the sour milk?
14. Give the derivation of the word *mordant*? (Consult dictionary.)
15. Give five different ways in which nitrogen from the atmosphere can be converted into nitric acid.

16. A solution of sodium sulfate has an alkaline reaction, while a solution of aluminum sulfate has an acid reaction. Explain.

17. Should you expect aluminum to decompose water under any conditions?

18. What weight of water of hydration is present in 1 kg. of potassium alum?

19. A certain bauxite ore was found to contain 90 per cent of  $\text{Al}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$ . What weight of aluminum could be obtained from 1 ton of the ore?

20. In what proportions by weight should cream of tartar and sodium bicarbonate be mixed in making baking powders?

21. Calculate the percentage composition of kaolinite.

22. 100 kg. of ammonium alum is heated until all the water of hydration is expelled. Calculate the weight of the residue.

23. In what proportions should aluminum sulfate and sodium bicarbonate be used in fire extinguishers (p. 501).

## CHAPTER XXXVII

### THE SILICATE INDUSTRIES

**The ceramic industries.** There are a considerable number of industries which are based upon the use of clay, sand, limestone, and feldspar in varying degree of purity, and in so far as they involve chemical transformations they are closely allied. To a greater or less extent they depend upon the formation of silicates from the materials named, the bases being chiefly oxides of sodium, potassium, calcium, magnesium, aluminum, and iron. These industries are often designated collectively as the *ceramic industries*. They may be roughly grouped into three classes, according to whether they are most intimately related to the manufacture of glass, cement, or clay products.

**Glass.** A glass is essentially a material which, on cooling from the state of a viscous liquid, has failed to crystallize and yet has become a rigid body. Pure quartz, when fused and cooled, is an example of the simplest of glasses. The ordinary commercial varieties of glass are *mixtures of various silicates, together with excess of silica*. When melted these all mix to form a homogeneous liquid, and when this is cooled it gradually hardens to a glass.

**Ingredients of glass.** The principal materials used in making glass are (1) sand and (2) suitable compounds of the desired metals. When these are heated together at a high temperature the silicates of the metals are formed, and it is these silicates, together with excess of the silica, that constitute the finished glass. In ordinary window glass and the cheaper kinds of bottle glass the chief materials employed are

sand, limestone, and sodium carbonate. When these are fused together there forms a sodium-calcium silicate glass approximating the formula  $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6 \text{SiO}_2$ . Any magnesium in the limestone will likewise form a silicate, displacing a part of the calcium in the above formula. Very pure materials must be used if a high-grade product is desired. Sand of snow-white purity is required, since the ordinary sand contains sufficient iron to impart an undesirable green color to the finished product.

We do not ordinarily think of window glass as soluble; yet chemical glassware such as test tubes and beakers, if made of glass of the above composition, would be acted upon by chemical reagents to such an extent as to render exact work impossible. Experiments have shown that a much more inert glass is obtained by using some boric acid along with the sand, so that the finished glass is a borosilicate of the different metals with excess of silica. Glass of this kind is therefore used in making chemical glassware. Thus, the glass known as *pyrex* is a sodium-calcium borosilicate containing an excess of silica. The optical glass used for making lenses of all kinds owes its brilliancy to lead silicate, formed by the addition of lead oxide to the glass mixture.

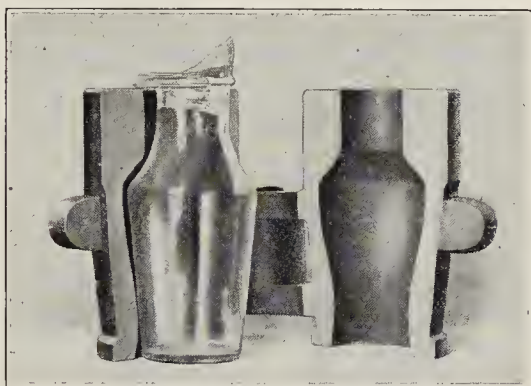


FIG. 202. Making a glass vessel by using a mold

**Molding and blowing glass.** The way in which the melted mixture is handled in the glass factory depends upon the character of the object to be made. Many articles, such as bottles, are made by blowing the plastic glass into hollow molds of the desired shape. The mold is opened, a lump of plastic glass on a hollow



rod is lowered into it, and the mold is then closed. By blowing into the tube the glass is forced into the shape of the mold. The mold is then opened (Fig. 202) and the object lifted out. The top of the object must be cut off at the proper place and the sharp edges rounded off in the flame. Bottles are now more often made by machinery, in which the bottle is blown by compressed air.

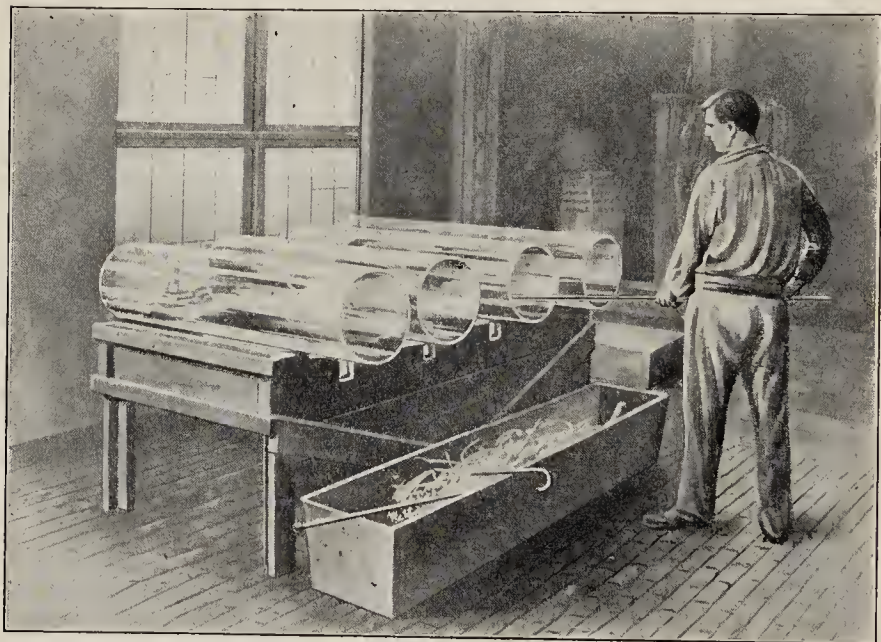


FIG. 203. Cracking the cylinders of glass lengthwise in order that they may be flattened out into the form of plates

Other objects, such as lamp chimneys, glasses, and beakers, are revolved while being blown in the mold, and have no ridge showing where the mold closes. Window glass has long been made by blowing cylinders of glass, 5 or 6 feet in length and 1 or 2 feet in diameter. These are cracked lengthwise (Fig. 203) and then heated until soft, when they are flattened out into sheets of glass much as a cylinder of paper, when cut lengthwise, will open out into a sheet of paper. While this comparatively expensive mouth-blown method of making window glass is still used to a certain extent, it is gradually being replaced by two other methods in which the work is more largely mechanical. (1) In one of these methods the cylinders of glass are made as follows:

A long, hollow rod *a* (Fig. 204), with a flattened end *b*, is lowered until the end is in contact with the molten glass in the pot *c*. The rod is slowly raised and at the same time sufficient air is forced through the rod to shape the thick molten glass clinging to the rod into cylindrical form, and to maintain this form until the glass hardens. By this process large cylinders can be made, some of them being 40 feet in length and 2 feet in diameter. They are cracked lengthwise and flattened out into sheets as explained above. (2) In the other still more recent method the glass is not blown at all, the viscous glass being drawn out directly by machines into glass sheets (Fig. 205). Each machine as now constructed has an annual productive capacity amounting to a sheet of glass 285 miles in length and 5 feet in width. This method is the least expensive of all and promises in time to displace the others.

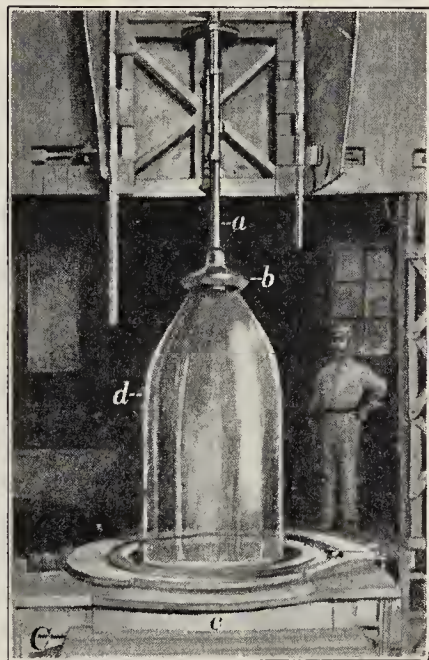


FIG. 204. First step in the making of window glass, — forming large cylinders of glass

**Color of glass.** The color of glass is usually due to the presence of colored metallic silicates. For example, ferrous silicate colors the glass green, while ferric silicate colors it yellow or brown. The green color can be changed to the less objectionable yellowish tint by the addition of manganese dioxide, which acts as an oxidizing agent, converting the ferrous compounds into ferric. Cobalt compounds form deep-blue silicates, and many other metals impart characteristic colors. Sometimes the metals themselves are added and form a colloidal dispersion. Copper and gold are added to glass to produce a rich, ruby-red color. Selenium also gives a beautiful red color to glass and is used

both to produce this color and to compensate for the green of ferrous silicate. Opaque, or milky, glasses are made by adding materials which remain suspended as solids in the melt, or which melt along with the glass but do not mix with it. In the latter case an emulsion is formed, and the turbid glass remains opaque on cooling. Fluorite, cryolite, bone ash, and tin oxide are used for producing these opaque glasses.

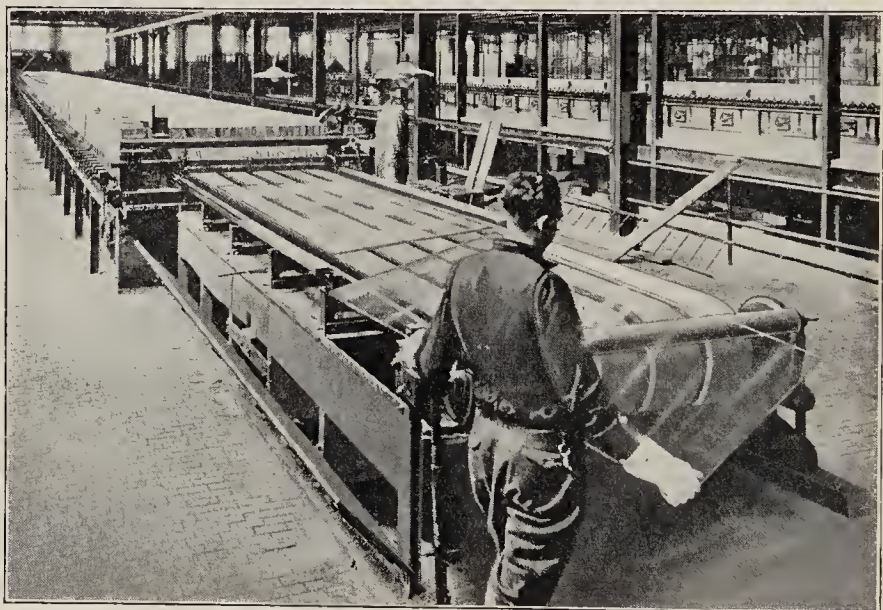


FIG. 205. Making window glass by drawing the viscous mass directly into sheets of glass

**Clay products.** The crudest forms of clay products, such as porous brick and drintile, have little chemistry involved in their manufacture. Natural clay is molded into the required form, dried, and then burned in a kiln, but not to a temperature at which the materials soften. In this process the pale-colored iron compounds in the clay are converted into highly colored compounds which give the usual red color to these articles. In making *vitified brick* the temperature is raised to the point at which the materials present begin to fuse, so that the brick is partially changed to a kind of glass.



**White pottery.** This term is applied to a variety of articles ranging from the crudest porcelain to the finest chinaware. While the processes used in the manufacture of the articles differ in details, fundamentally they are the same and may be described under three heads: namely, (1) the preparation of the body of the ware, (2) the process of glazing, and (3) the decoration.

**The body of the ware.** The materials used are kaolin, plastic clay, feldspar, and flint. This mixture is plastic and is worked into the desired shape by molds or on a potter's wheel (Fig. 206). The ware is then dried and burned in a kiln (Fig. 207) and in this form is known as *bisque*. This is usually porous and must therefore be glazed to render it nonabsorbent and give it a smooth surface.

**The glaze.** The glaze is a fusible glass which is melted over the surface of the body. The constituents of the glaze are silica, feldspar, and various metallic oxides, often mixed with a little boric oxide. These materials are finely ground and mixed with water to a paste. Sometimes they are first fused into a glass, which is then powdered and made into the paste. The *bisque* is dipped into the glaze paste, dried, and fired until the glaze materials melt and flow evenly over the surface.

**The decoration.** If the article is to be decorated, the design may be painted on the body before the article is glazed, or it may be painted on the glaze and the article fired again, the pigments melting into the glaze. In the former case the pigments used are, as a rule, metallic oxides of various colors, while in the latter case they are often colored glasses.



FIG. 206. The manufacture of pottery: molding the plastic material into form



**Cement.** The term *cement* as ordinarily used at present is applied to those mortars which possess the property of hardening in water as well as in air. These cements are mixtures of



FIG. 207. The manufacture of pottery : stacking the ware in the kiln for firing

silicates, usually very highly basic in character, and when ground fine and mixed with water they undergo complex reactions resulting in the formation of a hard, rocklike mass. A number of different classes of cements are known, the most important of which is called *Portland cement*.

**Composition of Portland cement.** The essential ingredients of Portland cement and their percentages are as follows :

$\text{SiO}_2$ , 19 to 26%.	$\text{Fe}_2\text{O}_3$ , 2 to 5%.	$\text{MgO}$ , 0 to 5%.	$\text{Na}_2\text{O}$ } 0 to 3%.
$\text{Al}_2\text{O}_3$ , 4 to 11%.	$\text{CaO}$ , 58 to 67%.	$\text{SO}_3$ , 0 to 2.5%.	$\text{K}_2\text{O}$ }

**Manufacture of Portland cement.** The materials most commonly employed are limestone or marl and clay or shale. In general, however, any substance may be used which furnishes the ingredients listed in the above table. Among the substances so used is blast-furnace slag, which is an impure calcium-aluminum silicate.

The materials are coarsely ground and then mixed together in the proper proportions and finely pulverized. The resulting mixture is run into a furnace and burned to a temperature just short of fusion; at this temperature it vitrifies, forming a grayish mass known as *clinker*. Finally, the clinker is ground to a fine powder. Gypsum is often added in the process; this acts as a negative catalyzer, retarding the hardening, or setting, of the cement.

**The setting of cement.** The reactions which take place upon the addition of water to cement, and which result in the formation of a hard, rocklike mass, are not thoroughly understood. The constituents of the cement apparently undergo hydrolysis when they come in contact with water. The resulting compounds unite with water, producing hydrates. These hydrates are crystalline in character and form a hard, compact mass.

**Growing importance of cement.** Cement has come into use for a great variety of purposes. It is often used in place of mortar in the construction of brick buildings. Mixed with crushed stone and sand it forms *concrete*, which is used in foundation work for buildings and street paving. It is also used in making artificial stone, terra-cotta trimmings for buildings, artificial-stone walks and floors, fence posts, and the like. It is being used more and more for making articles which were formerly made of wood or stone, and the entire walls of buildings are sometimes made of cement blocks or concrete. Iron rods or wire are often embedded in the concrete before it sets, to give it greater strength, and the resulting material is called *reinforced concrete*.

### EXERCISES

1. In the manufacture of pottery why is the glaze made more fusible than the body of the ware?
2. Suppose that the glaze and the body expand and contract at different rates with changes in temperatures, what will be the result?
3. What is the meaning of the word *vitrify*?
4. What is a catalyzer? What is a *negative* catalyzer?
5. Why can cement be used as mortar in colder weather than ordinary mortar?
6. What weight of kaolin will result from the weathering of 1 ton of feldspar?
7. Calculate the percentage composition of kaolinite.
8. In what proportion must raw materials be mixed so as to secure a glass of the composition expressed by the formula  $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6 \text{SiO}_2$ , assuming that the limestone used is 98 per cent calcium carbonate?

## CHAPTER XXXVIII

### THE PURIFICATION AND THE SOFTENING OF NATURAL WATERS

**Natural waters never chemically pure.** In the chapter on water it was pointed out that natural waters are never chemically pure,—that they always contain more or less mineral matter and organic matter dissolved from the rocks and the soil with which the waters come in contact. If, therefore, we wish to obtain chemically pure water from natural waters, it is necessary to separate the foreign matter present. This can be done by the process of distillation, as already explained. For most purposes, however, it is not necessary and often not desirable to use chemically pure water. Thus, to render natural waters good for drinking purposes it is only necessary to remove the organic matter, or often merely to destroy the vitality of any disease-producing microorganisms present, for the small amount of mineral matter ordinarily present in such waters is in no way deleterious to health.

**Importance of purifying water.** An adequate supply of wholesome drinking water is of the utmost importance to a community, and the problem of securing such a supply becomes increasingly difficult as the population increases. Our cities and many of our towns find it necessary to take their water supply from rivers and lakes. With increasing population it is impossible to keep such waters from becoming contaminated with sewage and other organic matter, which are natural carriers of disease-producing germs.

**Effect of water purification on disease.** Fig. 208 shows the effect of water purification in diminishing the deaths due to typhoid fever in a typical city (Columbus, Ohio). Before the water was

purified, typhoid fever was always prevalent; for example, in 1904 (Fig. 208) there were 135 deaths from this disease for each 100,000 inhabitants. After the construction of a water-purification plant, in 1909, the deaths due to this disease fell off greatly, amounting in 1920 to only 3 for each 100,000 of population; and at present the disease is almost unknown in this city. The proper purification of the water supply is therefore a problem of the greatest importance in maintaining the health of a city.

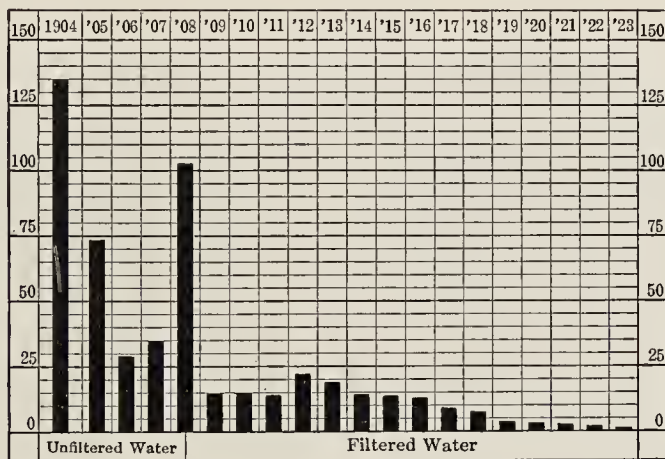


FIG. 208. Chart showing relation between water purification and the prevalence of typhoid fever. Figure gives death rate per 100,000 population

**Methods of purifying water on a large scale.** Such processes as boiling and distillation are manifestly impracticable when it comes to dealing with the large quantities of water necessary to meet the demands of our cities and towns. In Columbus, Ohio, for example, the city water system is drawn upon for an average of 30,000,000 gallons daily, while in Chicago the amount is 800,000,000 gallons. A number of different methods of purifying water on a large scale are now in use. These methods differ in detail, but all are alike in that the water is treated with chlorine, which destroys any microörganisms present. The amount of chlorine added varies from 2 to 5 pounds per 1,000,000 gallons of water. Following is a discussion of the different methods used:



1. *Treatment with chlorine alone.* This is the simplest method, but it can be effectively employed only when the natural water used is clear, as is the case in Chicago and New York. Ordinarily the pure chlorine is added directly (Fig. 209), although in some instances bleaching powder is used as a source of chlorine.

2. *Filtration through slow sand filters and subsequent treatment with chlorine.* These filters are constructed of sand and gravel, as shown in Fig. 210. Some of the impurities are strained out

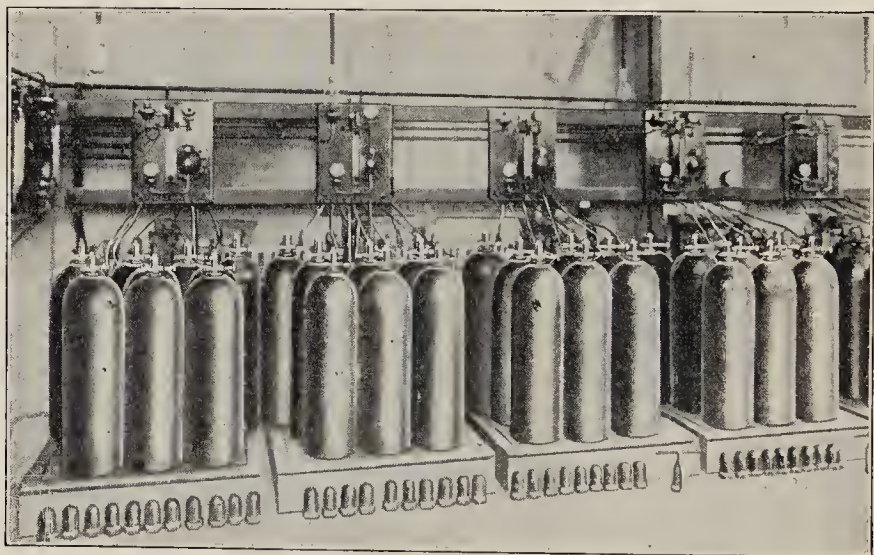


FIG. 209. Purification of water supply of New York City by adding chlorine to the impure water

by the filter, while others are decomposed by the action of certain kinds of microorganisms which collect in a jellylike layer on the surface of the filter. Chlorine is added to the filtered water as an extra precaution.

3. *Treatment with aluminum sulfate (or ferrous sulfate), filtration, and subsequent treatment with chlorine.* Most of our natural waters are basic in character. When aluminum sulfate is mixed with such waters, hydrated aluminum oxide (aluminum hydroxide) is formed (p. 498) as a colloidal dispersion throughout the water. This slowly coagulates and, as it settles,

carries down with it any suspended matter present (Fig. 211), including microorganisms and coloring materials. After the precipitate has settled, the supernatant water is drawn off and run through rapid sand filters. It is then treated with a small amount of chlorine as a final precaution. The rapid sand filters are made of sand and gravel (H, Fig. 212). They are largely replacing the slow sand filters, since they are much less expensive and are equally effective when used with water which has been treated with aluminum sulfate as described above.

**Softening of hard waters.** Most of the natural waters have varying percentages of compounds of calcium and of magnesium derived from contact with various rocks. All such waters are called *hard*. These hard waters are objectionable in many ways. For example, when they are used for

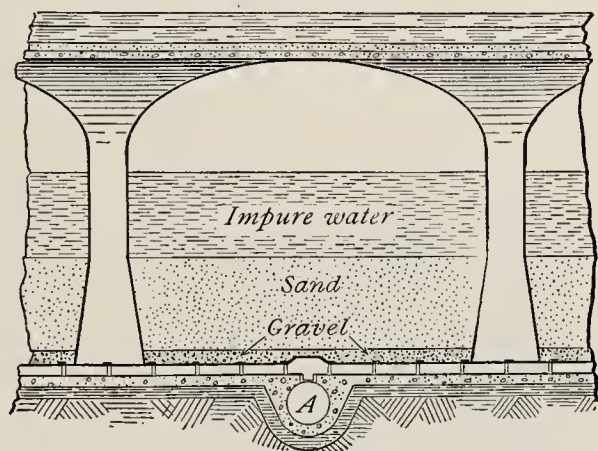


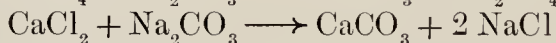
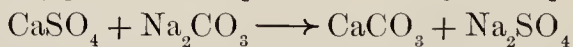
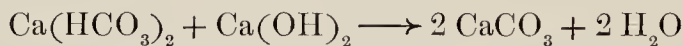
FIG. 210. A covered slow sand filter for purifying water on a large scale

The water filters through the sand and gravel and passes into the porous pipe *A*, from which it is pumped into the city mains

cleansing purposes much larger quantities of soap are required than with soft waters, and if they are used in steam boilers, deposits are formed, known as boiler scale (p. 481). Hence some cities not only purify their water but soften it as well.

The method used for accomplishing these two ends is the same as method 3, given above, for purifying waters, except that along with the aluminum sulfate certain quantities of calcium hydroxide and sodium carbonate are added. The calcium and magnesium in hard waters are present either in the

form of acid carbonates or of chlorides and sulfates. That portion of the calcium and magnesium present as acid carbonate is precipitated by the calcium hydroxide added, while that present as chloride and sulfate is precipitated by the sodium carbonate. These reactions are expressed in the following equations (using calcium as the example, since calcium and magnesium act in the same way):



The calcium and magnesium carbonates formed are practically insoluble in the resulting water and settle out as the water

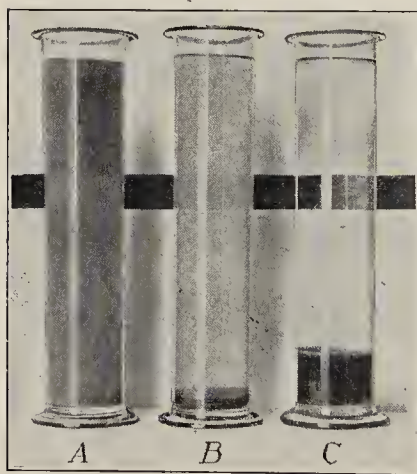


FIG. 211. Purification of water by aluminum sulfate

The cylinder *A* contains impure water. *B* is a similar cylinder of water to which some aluminum sulfate has been added. The appearance of the water after the settling of the impurities is shown in *C*

slowly flows through reservoirs known as *settling basins* (Fig. 212). It is evident, from the equations given above, that waters softened by this process will contain sodium sulfate and sodium chloride, but the presence of these salts is not objectionable. Some idea of the economy resulting from the softening of the city water supply may be inferred from the fact that it is estimated that the softening of the city water in Columbus, Ohio, has effected a saving in soap alone amounting annually to \$250,000. The industrial importance of a purified water

supply may be realized from the fact that the New York Central Railway expends nearly a million dollars annually in purifying and softening its water supply.

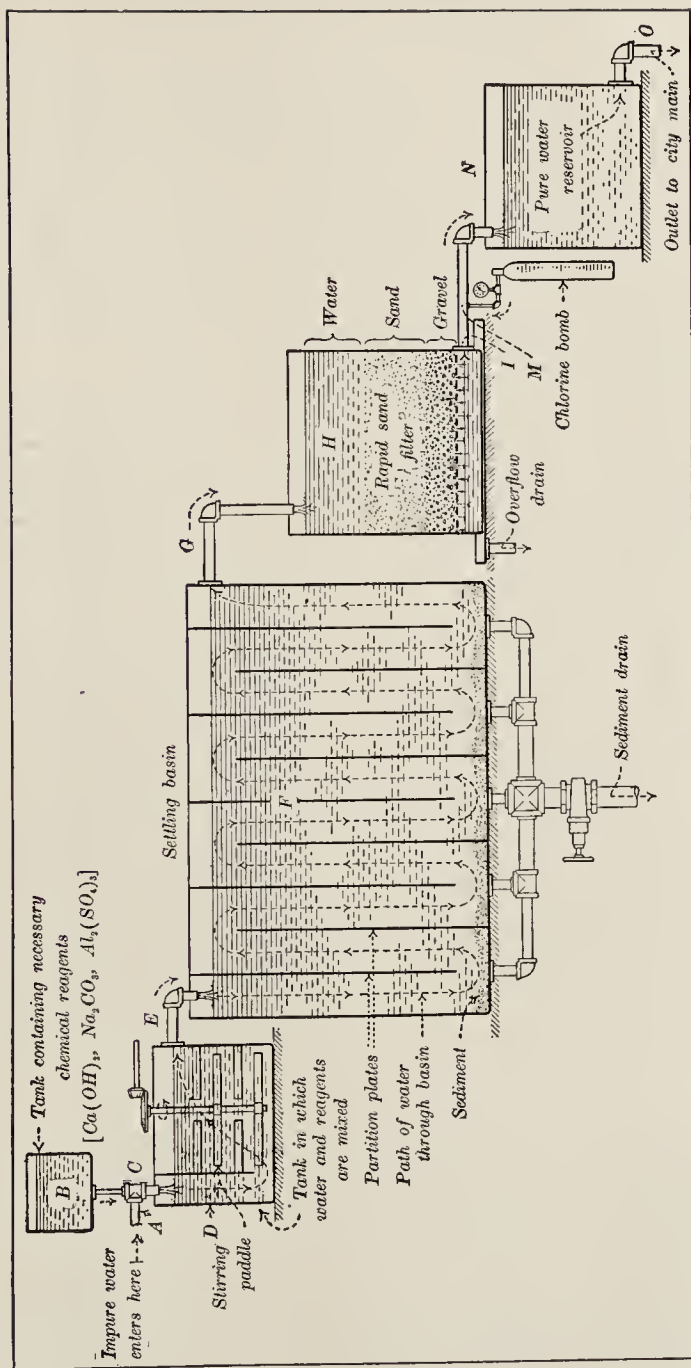


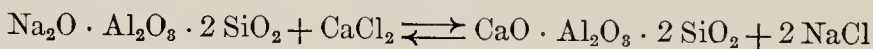
FIG. 212. Diagram showing the essential parts of a plant for softening and purifying the water supply of a city. The impure, hard water enters at *A*, and at *C* meets with the necessary purifying reagents entering from the tank *B*. The two flow into the mixing tank *D* and are thoroughly mixed by the stirring device. The mixture then flows into the settling basin *F*, and as the water slowly passes through this the solids formed by the action of the purifying reagents upon the water and its foreign ingredients settle to the bottom and are drawn off from time to time. The purified water then flows through *G* into the rapid sand filter *H*. As it passes out of this the necessary chlorine is added at *M*. The water then flows into the pure-water reservoir and from this into the city mains.



**Details of the process.** Fig. 212 shows how the processes of purifying and softening water are carried out on a large scale.

**A simple method for purifying small quantities of drinking water.** The United States Army Medical School recommends the following simple method as one not only effective but suitable for soldiers and campers. It is only necessary to add one or at most not more than two drops of the ordinary druggist's *tincture of iodine* (p. 310) to one quart of water. The mixture is shaken and set aside for half an hour. The iodine will destroy all the harmful micro-organisms and render the water safe for drinking.

**The zeolite process for softening water.** The name *zeolite* is given to a mixture of complex sodium aluminum silicates found in nature and also prepared for use in softening water on a moderately large scale. This substance is characterized by the fact that the sodium present in the silicates is replaced by calcium and magnesium when brought in contact with solutions of these compounds:



If now a saturated solution of sodium chloride is allowed to flow over the resulting calcium compound, the reaction is reversed (mass action, p. 240) and the zeolite regenerated. In other words, the reaction is reversible and may be made to go in either direction by increasing the mass of the appropriate compound. In softening water by this process the zeolite is placed in a long drum and the water passed through the drum. The apparatus is built in duplicate, so that the material in the one drum may be regenerated while that in the other drum is being used for softening the water. It is evident that water softened in this way will contain sodium salts, but these have no effect on soap.

### EXERCISES

1. Is it ever possible to remove calcium from a hard water by the addition of more calcium? If so, give the conditions under which this apparent anomaly can be effected.

2. A certain city uses 30,000,000 gal. of water daily, and 100 gal. of the water contains 120 g. of calcium acid carbonate and 30 g. of calcium sulfate. What weights of calcium hydroxide and sodium carbonate are required to soften the daily water supply?

## CHAPTER XXXIX

### THE IRON FAMILY

	SYMBOLS	ATOMIC WEIGHT	DENSITY	MELTING POINT	OXIDES
Iron . . . . .	Fe	55.84	7.86	1535°	FeO, Fe <sub>2</sub> O <sub>3</sub>
Cobalt . . . . .	Co	58.94	8.90	1480°	CoO, Co <sub>2</sub> O <sub>3</sub>
Nickel . . . . .	Ni	58.69	8.90	1452°	NiO, Ni <sub>2</sub> O <sub>3</sub>

**The family.** The elements iron, cobalt, and nickel bear a relation to one another which is different from that existing among the members of any other family as yet considered. Their atomic weights are very close together, and in the periodic table they are placed in one family, not because the plan of arrangement brings them together, but because they are so similar (p. 260) and evidently constitute a natural family.

Iron is noteworthy as the first metal to be described in detail which exerts two different valences and forms two series of salts. In the *ferrous salts* the iron is bivalent, and in many respects ferrous salts resemble those of magnesium; in the *ferric salts* the iron is trivalent, the ferric salts resembling those of aluminum. It is therefore appropriate to consider iron at the present time. It is also worthy of note that the metals which remain to be considered are isolated by reduction of their oxides or from their sulfides, and not by electrolytic methods.

These three metals differ from all those so far studied in that they are magnetic, and the cheapest of these, namely iron, is the metal used in the construction of magnets.

## IRON

**Occurrence.** The element iron has long been known, since its ores are very abundant and it is not difficult to prepare the metal from them in fairly pure condition. It occurs in large deposits as oxides, sulfides, and carbonates, and in smaller quantities in a great variety of minerals. Indeed, very few rocks or soils are free from small percentages of iron. It is a constituent of the chlorophyll of plants and the hæmoglobin of the blood of animals, and therefore plays an important part in life processes. Many meteorites are largely iron, usually alloyed with a little nickel.

**Preparation of pure iron.** Pure iron may be prepared in the form of a fine powder by heating the oxide in a current of hydrogen, though the product contains adsorbed hydrogen unless the process is carried out at a higher temperature. It may be obtained in coherent masses by the electrolysis of ferrous sulfate between iron electrodes. To prevent the adsorption of hydrogen, which makes the metal hard and brittle, it is necessary to conduct the electrolysis at about  $100^{\circ}$  and to add some calcium chloride to the electrolyte. By such methods Burgess has obtained iron said to be 99.98 per cent pure. Iron of a high degree of purity is now prepared on a large scale as described later in the chapter.

**Properties of pure iron.** Pure iron is a silvery metal having a density of 7.86 and a melting point of  $1535^{\circ}$ . It is ductile and malleable and is almost as soft as aluminum. It is especially well adapted to the manufacture of electromagnets, since it acquires and loses magnetic properties much more rapidly than do the ordinary varieties of iron. It is not acted upon to any extent by air and hence is adapted to purposes for which resistance to corrosion is desired.

**The iron of commerce.** Iron differs from most of the other metals used in the industries in that the pure metal is rarely obtained and is of limited application, while that which contains

small percentages of other elements exhibits a wide variety of properties and is of the greatest importance. Carbon is always present in quantities which range from mere traces up to 7 per cent. According to the conditions under which the metal is produced, this carbon may be in the form of graphite scattered through the iron, or as a solid solution of carbon in iron, or in combination with the iron in the form of a carbide. The most important of these carbides has the formula  $\text{Fe}_3\text{C}$  and is a hard, brittle substance known as *cementite*. Manganese and silicon, together with traces of phosphorus and sulfur, are also present.

The properties of iron are much modified by the percentages of these constituents, by their form of combination in the iron, and by the treatment of the metal during its production from the ore. Accordingly many varieties of iron are recognized in commerce, the chief of which are *cast iron*, *wrought iron*, and *steel*.

**The metallurgy of iron.** The problem to be solved in the production of commercial iron is (1) to obtain a metallic alloy of the requisite chemical composition and physical properties and (2) to produce it on a very large scale. The development of the huge modern furnaces has demanded a wonderful application of chemical knowledge to a definite purpose and a no less wonderful engineering skill in securing the present great scale of production. To understand the processes to be described it will be necessary to remember constantly that large and rapid production is fully as necessary as great purity.

**Materials used in metallurgy of iron.** Four different classes of materials are used in the metallurgy of iron:

1. **Iron ore.** The ores most frequently employed are *hematite* ( $\text{Fe}_2\text{O}_3$ ); *siderite* ( $\text{FeCO}_3$ ); *limonite* ( $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ); *magnetite* ( $\text{Fe}_3\text{O}_4$ ). As mined for use all ores contain earthy matter and often sulfides and phosphates as well.

While iron ore is mined in a number of different localities in the United States, the great center of production is in the neighborhood of Lake Superior in the states of Minnesota



and Michigan, the ore being chiefly *hematite*. Large quantities are also mined near Birmingham, Alabama. Normally about 60,000,000 tons of iron ore are mined in the United States annually.

2. **Carbon.** Carbon in some form is necessary both as a *fuel* and as a *reducing agent*. In former times wood charcoal was used to supply the carbon, but now coke is almost universally employed.

3. **Hot air.** To maintain the high temperature that is required for the reduction of iron, a very active combustion of fuel is necessary. This is secured by forcing a strong blast of *hot air* into the lower part of the furnace during the reduction process.

4. **Flux.** All the materials which enter the furnace must leave it again, either in the form of gases or as liquids. The *iron* is drawn off as the liquid metal after its reduction, the *oxygen* with which it was combined escaping as oxide of carbon. The ore is rarely a pure compound of iron but contains certain foreign matters — generally silicates. To secure the removal of these impurities charged into the furnace along with the ore, materials are added to the charge which will combine with the impurities in the ore, forming a liquid at the temperature of the furnace. The material added for this purpose is called the *flux*, and the liquid produced by the interaction of the flux and impurities is called *slag*.

**The slag.** The slag is a variety of difficultly fusible glass, being essentially a calcium-aluminum silicate. If the ore is rich in silica, as is usual, limestone is used as a flux; if the ore contains limestone, silica or feldspar is used; if the ore is very pure, both constituents must be added as flux.

The formation of slag converts the oxides of calcium, magnesium, aluminum, and silicon contained in the ore into the liquid state, and not only does this make the removal of these materials easy, but the liquid is a necessity for other reasons. It is a medium in which the little droplets of iron run together

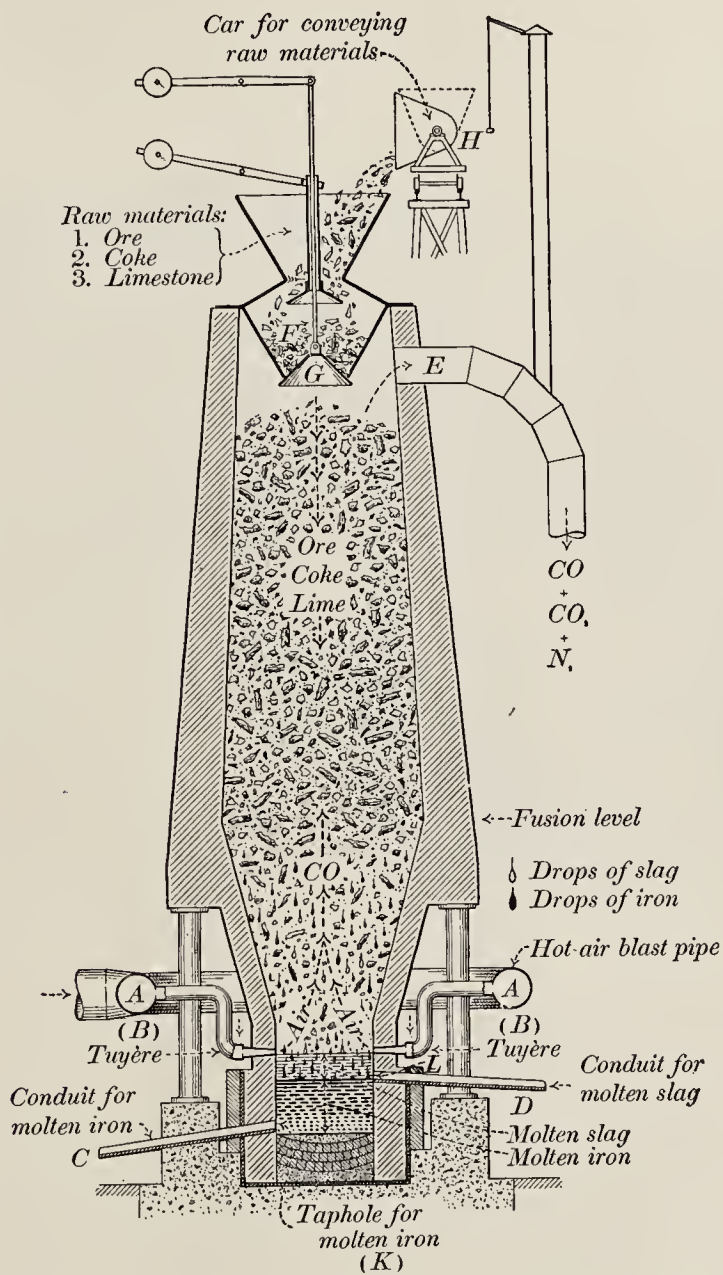


FIG. 213. Vertical section of a typical blast furnace

into one large mass; it keeps the contents of the furnace liquid and so prevents clogging; it floats over the collected iron and prevents its oxidation. In every operation in which iron is melted a slag must be provided.

**Cast iron (pig iron).** Ordinarily the first step in the manufacture of any variety of commercial iron is the production of *cast iron* or, as often called, *pig iron*. The ores are mixed with a suitable flux and are reduced by heating with coke.

**Blast-furnace process.** The reduction is carried out in a large tower called a blast furnace (Fig. 213). This is usually about 80 ft. high and 20 ft. in internal diameter at its widest part, narrowing somewhat toward both the top and the bottom. The walls are built of steel and are lined with fire brick. The base is girdled with a pipe *A, A*, through which a blast of hot air is forced. Leading from this are smaller pipes *B, B*, called *tuyères*, which conduct the blast of hot air into the furnace. At the base of the furnace is a tap hole *K* for the molten iron, through which the liquid metal can be drawn off from time to time. There is also a second opening *L*, somewhat above the first, through which the excess of molten slag is drawn off. The top is closed by a movable trap *G* called the *bell*, and through this the materials to be used are introduced. The gases resulting from the combustion of the fuel and the reduction of the ore, together with the nitrogen of the air admitted through the tuyères, escape through pipe *E*. These gases have a temperature of about  $300^{\circ}$  and contain a sufficient percentage of carbon monoxide to render them combustible; they are accordingly utilized for heating the blast of air admitted through the tuyères and as fuel for the engines.

Charges consisting of coke, ore, and flux in proper proportion are at intervals introduced into the furnace through the bell. At the bottom of the furnace the coke burns fiercely in the hot-air blast, forming carbon dioxide, which is at once reduced to carbon monoxide as it passes over the highly heated carbon.

The temperature of the furnace at the point at which the hot air enters is about  $1600^{\circ}$ , but gradually decreases toward the top of the furnace, at which it is only from  $300^{\circ}$  to  $400^{\circ}$ . Reduction of the ore begins at the top of the furnace through the action of the carbon monoxide. As the ore slowly descends, the reduction

is completed and the resulting iron melts and collects as a liquid in the bottom of the furnace, the lighter slag floating above it. After a considerable quantity of iron has collected, the slag is drawn off, and the iron is run out into large buckets and taken

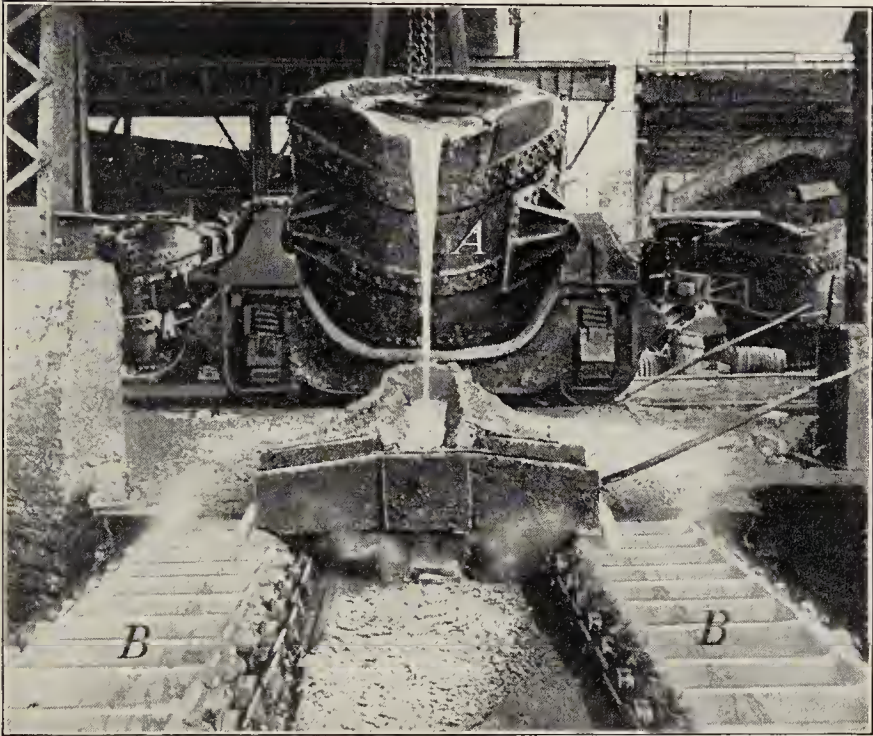


FIG. 214. Pouring molten cast iron (A) into iron troughs or molds (B, B) lined with lime

These troughs are connected so as to form an endless chain or belt. The molten iron in each trough solidifies by the time it reaches the farthest point; and as the chain reverses, the solid pieces of iron fall into cars placed beneath the chain

to the converters for the manufacture of steel; or it is run into iron troughs or molds lined with lime and connected in the form of an endless chain, as shown in Fig. 214. The process of producing cast iron is a continuous one, and when the furnace is once started, it is kept in operation for months without interruption or until the furnace requires repairing. The iron is withdrawn at intervals of about six hours. In practice a number of furnaces are usually operated together.



**The production of cast iron.** The United States produces about half the cast iron of the world. Some idea of the growth of the iron industry in the United States may be inferred from the increase in the production of cast iron, for it is the raw material from which all other forms of iron are made. The production in tons for the years stated is, in round numbers, as follows :

1850 . . . . .	563,000	1890 . . . . .	9,000,000
1860 . . . . .	821,000	1900 . . . . .	14,000,000
1870 . . . . .	1,665,000	1910 . . . . .	27,000,000
1880 . . . . .	3,835,000	1920 . . . . .	37,000,000

**Properties of cast iron.** The product of the blast furnace is called *cast iron*. It varies considerably in composition but always contains over 2 per cent of carbon, variable quantities of silicon, and at least traces of phosphorus and sulfur. Two extreme varieties of cast iron are recognized: *gray* iron and *white* iron. In gray iron the carbon is present partly in the form of *cementite* ( $\text{Fe}_3\text{C}$ ) and partly as *graphite*, which gives the metal its gray color. In white cast iron almost all the carbon is in the combined state in the form of cementite. Between these two extreme types there are all intermediate varieties. Cast iron is hard and brittle and melts at about  $1100^\circ$ . It cannot be welded or forged but is easily cast in sand molds. It is rigid but not elastic, and its tensile strength is small. It is used for making castings and in the manufacture of other varieties of iron. Cast iron, especially those grades of high silica content, is not acted upon by acids to the same extent as the purer grades of iron and so is used in making vessels for concentrating acids and for similar purposes.

**Wrought iron.** Wrought iron is made from cast iron by burning out most of the carbon, silicon, phosphorus, and sulfur which it contains.

**The puddling furnace.** The process is carried out in a *puddling furnace*. The floor of the furnace is covered with a layer of iron oxide, and on this is placed the charge of cast iron, together with some suitable flux (usually limestone). The fuel is burned in a

fire box at the side of the furnace, and the flame is led over the charge of cast iron, the heat being reflected down upon it by a low, arching roof. The iron is soon melted, and the phosphorus and silicon are oxidized by the iron oxide, forming acid anhydrides, which combine with the flux or with the iron oxide to form a slag. The carbon and sulfur are also oxidized and escape as carbon dioxide and sulfur dioxide. As the iron is freed from other elements it becomes pasty, owing to the higher melting point of the purer iron, and in this condition forms small lumps, which are raked together into a larger one. The large lump is then removed from the furnace and rolled or hammered into bars, most of the slag being squeezed out in this process.

**Properties of wrought iron.** Wrought iron has a fibrous structure, being composed of fibers of pure iron (*ferrite*) separated by a small percentage of slag. The ferrite present contains less than 0.3 per cent of carbon and small quantities of other elements. Wrought iron is soft, malleable, and ductile. While its tensile strength is greater than that of cast iron, it is less than that of most steel. Its melting point is much higher than that of cast iron. Wrought iron is no longer produced to the same relative extent as in former years, since soft steel can be made at less cost and has almost the same properties.

**Steel.** Steel, like wrought iron, is made from cast iron by burning out a part of the carbon, silicon, phosphorus, and sulfur, but the processes used are quite different from that employed in the manufacture of wrought iron. Nearly all the steel of commerce produced in the United States is made by one of two general methods known as the *acid Bessemer process* and the *basic open-hearth process*.

**Acid Bessemer process.** In the acid Bessemer process the furnaces used are lined with *silica*, which, it will be recalled, is an *acid anhydride*. These furnaces remove from the cast iron the carbon and silicon but not the phosphorus and sulfur. The process is therefore employed when the cast iron to be used is low in phosphorus and sulfur.

**Details of operation of Bessemer process.** This process, invented about 1860, is carried out in great egg-shaped crucibles called *converters* (Fig. 215), each one of which will hold as much as 15 tons of steel. The converter is built of steel and lined with silica. It is mounted on trunnions, so that it can be tipped over on its side for filling and emptying. One of the trunnions is hollow, and a pipe connects it with an air chamber (*A*), which forms a false bottom to the converter. The true bottom is perforated, so that air can be forced in by an air blast admitted through the trunnion and the air chamber.

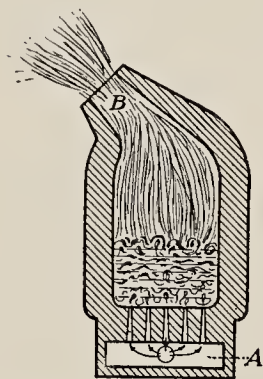


FIG. 215. Vertical section showing details of a Bessemer converter

White-hot liquid cast iron from a blast furnace is run into the converter through its open, necklike top *B*, the converter being tipped over to receive it; the air blast is then turned on, and the converter is rotated to a nearly vertical position. The carbon manganese and silicon in the iron are rapidly oxidized (first the silicon and manganese and then the carbon), the oxidation being attended by a brilliant flame (Fig. 216). The heat of the reaction, largely due to the combustion of silicon, keeps the iron in a molten condition. The air blast is continued until the character of the flame shows that all the carbon has been burned away. The process requires on the average about ten minutes, and when it is complete the desired quantity of carbon (generally in the form of high-carbon iron alloy) is added and allowed to mix thoroughly with the fluid. The converter is then tilted and the steel run into molds, and the ingots so formed are hammered or rolled into rails or other objects. The process must be conducted very rapidly, for as soon as the silicon and carbon have been burned there is no way to keep the iron from cooling, and it must be poured at once.

**Basic open-hearth process.** In the basic open-hearth process the lining of the furnace is made of limestone or dolomite, both of which act as *bases*. In such furnaces the phosphorus and sulfur are both removed, as well as the silicon and carbon. The presence of more than traces of phosphorus and

sulfur in the finished steel renders the metal so brittle that it is worthless for most purposes. The open-hearth process, therefore, possesses a great advantage over the acid Bessemer process in that it makes it possible to utilize iron ores (or cast iron obtained from them) that contain appreciable quantities of phosphorus and sulfur. The operation does not need to be hastened, and steel of any desired composition can be produced.

**Details of the open-hearth process.** Fig. 217 shows the simpler parts of the type of furnace used in this process. The hearth of the furnace is about 40 ft. in length, 12 ft. in width, and 2 ft. in depth, and is lined with limestone or dolomite (*A, A*). Either gas or sprayed oil is used as fuel, and finely powdered coal is now being employed. Below

the furnace is placed a checkerwork of brick so arranged that the hot products of combustion escaping from the furnace may be conducted through it, thus heating the bricks to a high temperature. Both the air necessary for combustion and the gaseous fuel (unless decomposed by heating, as in the case of natural gas and sprayed oil) are preheated by passing them over the hot bricks, so that the temperature reached during combustion is greatly increased.

The gas entering through *C* comes in contact at *D* with the hot air entering through *B*, and a vigorous combustion results, the

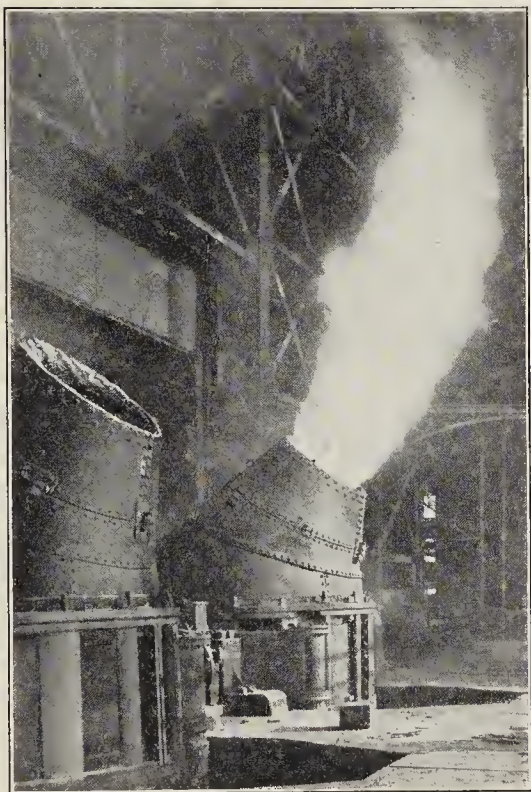


FIG. 216. View of a Bessemer converter in action



flame passing above and over the cast iron and lime with which the furnace is charged. The products of combustion escape through *E* and *F*. At the temperature reached, the carbon in the cast iron is removed in the form of the oxide, the escaping gas giving the melted metal the appearance of boiling. The silicon, phosphorus, and sulfur unite with oxygen to form acid anhydrides; these combine with the lime to form a slag, and this rises to the surface of the melted charge and is easily removed.

When a test shows that the desired percentage of carbon is present, the melted steel is run into large ladles and then into

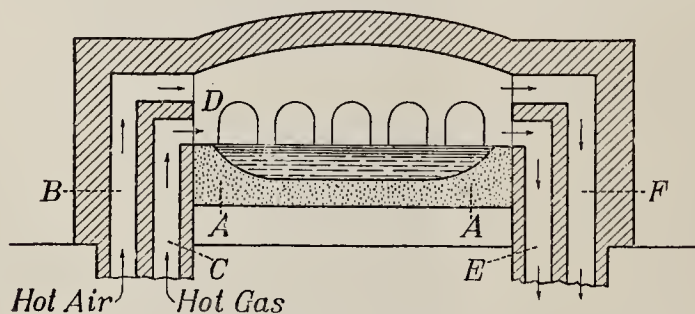


FIG. 217. Vertical section of an open-hearth surface

molds. An average furnace produces about 50 tons of steel in a given charge, approximately eight hours being required in the process. At present by far the largest amount of steel produced in the United States is made by this process.

**Tool steel or crucible steel.** Steel designed for use in the manufacture of edged tools and similar articles should be relatively free from silicon and phosphorus, but should contain from 0.5 to 1.5 per cent of carbon. The percentage of carbon should be regulated by the exact use to which the steel is to be put. Steel of this character is usually made in small lots from either Bessemer or open-hearth steel in the following way.

A charge of melted steel is placed in a large crucible and the calculated quantity of pure carbon is added. The carbon dissolves in the steel, and when the solution is complete the metal is poured out of the crucible. This is sometimes called crucible steel.

**Electrothermal metallurgy of steel.** An increasing quantity of high-grade tool steel is being produced in electrical furnaces. The furnace is heated by electrical energy, and a large quantity of steel can be kept melted in these furnaces as long as may be desired. The electrical current is used merely to produce heat, so that the process is not dependent upon

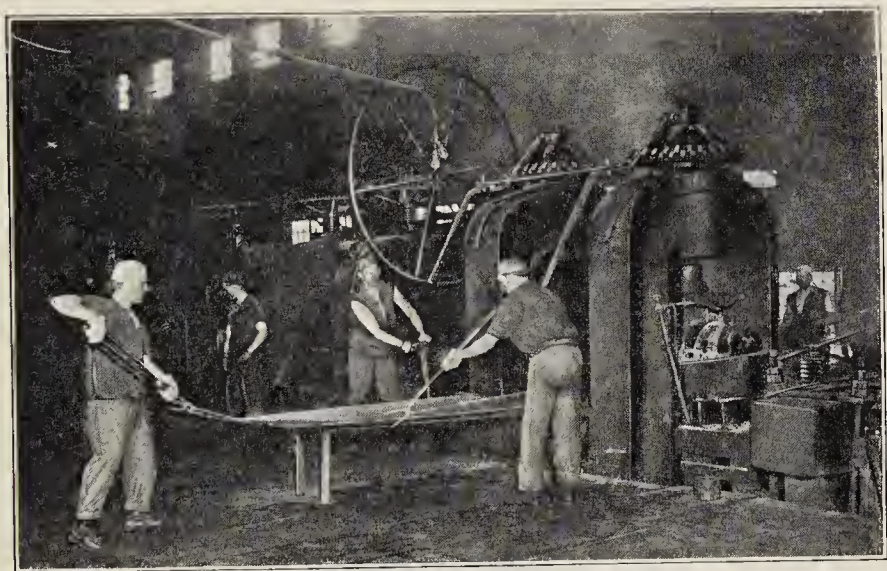


FIG. 218. Rolling low-carbon steel into sheets

electrolysis. This method is almost identical with the open-hearth method, save in the way in which the heat is supplied, and produces the same kind of steel as does the latter method.

**Properties of steel.** Steel contains from a trace up to 2 per cent of carbon, less than 0.1 per cent of silicon, and not more than traces of phosphorus and sulfur. When desired, a product containing as high as 99.85 per cent of iron can be produced by the open-hearth method. Such steel is very soft but resists rust. As the percentage of carbon increases, the steel becomes harder and less ductile. Steel is malleable and can be rolled into sheets (Fig. 218). It is also cast in molds and forged into desired shapes.

**The hardening and tempering of steel.** When steel containing from 0.5 to 1.5 per cent of carbon is heated to a relatively high temperature and then cooled suddenly by plunging it into cold water or oil, it becomes very hard and brittle. When gradually reheated and then allowed to cool slowly this hardened steel becomes softer and less brittle, and this process is known as *tempering*.

**Control of tempering.** By properly regulating the temperature to which the steel is reheated in tempering, it is possible to obtain any condition of hardness demanded for a given purpose, as for making springs or cutting-tools. Steel assumes different color tints at different temperatures, and by these the experienced workman can tell when the desired temperature has been reached. Lake gives the following temperatures for the tempering of tools:

220° . . . . .	paper cutters, wood-engraving tools
240° . . . . .	knife blades, rock drills
260° . . . . .	hand-plane cutters and cooper's tools
275° . . . . .	axes, springs
290° . . . . .	needles, screw drivers
300° . . . . .	wood saws

**Alloy steels.** As we have seen (p. 523), small quantities of carbon greatly modify the properties of iron, and equally marked effects may be produced by a great many other elements. Accordingly, to secure a steel with the requisite properties, suitable percentages of these elements are added to the steel just before it is run out of the furnace. The elements most frequently added are manganese, silicon, nickel, chromium, tungsten, vanadium, and titanium, and steel containing an appreciable percentage of any of these elements is called an *alloy steel*. The alloy element is added in the form of a rich alloy of iron, such as *ferrochromium* or *ferromanganese*.

The approximate percentage of metals other than iron present in some of the principal steel alloys, as well as the chief uses of the alloys, is as follows:



3.5% nickel . . . . .	armor plate, nickel steel
3.5% nickel and 2.5% chromium . . . . .	armor plate and projectiles
12.0% manganese . . . . .	burglar-proof safes
5.0% chromium and from 8 to 24% tungsten . . . . .	high-speed lathe tools
0.1% titanium . . . . .	car rails and steel castings
0.2% vanadium, 3.5% nickel, 0.75% chromium, and 0.4% manganese . . . . .	automobile springs and axles
12-15% silicon (duriron and tantiron) . . . . .	retorts for distilling acids, electrodes
70% cerium . . . . .	gas and cigar lighters
0.1% vanadium . . . . .	automobile parts

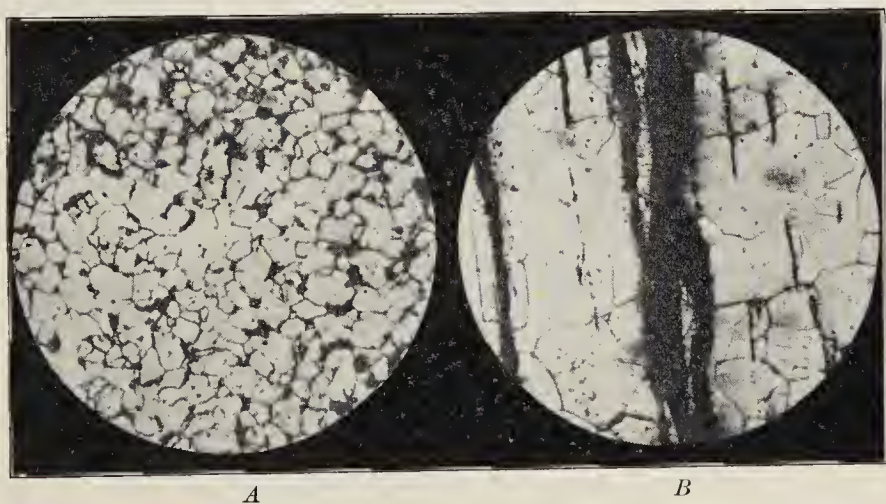


FIG. 219. Microphotographs (magnified 100 diameters) of samples of (A) low-carbon steel and (B) wrought iron

These two samples have nearly the same percentage composition, but their different methods of manufacture have resulted in entirely different physical structures with corresponding differences in properties

**Steel purifiers.** The great difficulties in securing a good steel are (1) to accomplish the complete reduction of the oxide and (2) to prevent the solution of gases which cause blowholes as the casting solidifies. These difficulties are avoided, as far as possible, by adding to the steel, at the close of the operation, certain elements which will combine with the oxygen and the dissolved gases. The compounds formed pass into the slag,



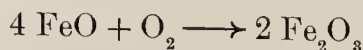
and almost none of the added element remains in the finished product. Aluminum is used to a large extent for this purpose, as are also vanadium and titanium. Such elements are called *purifiers* or *scavengers*.

**Metallography.** We have seen that the varieties of iron differ not only in chemical composition but also in physical structure. Much information concerning the structure of any sample of iron (and other metals as well) can be obtained from microphotographs taken of carefully prepared specimens of the different varieties of iron. To prepare these a cross section of the sample is made and polished. This is then etched with some reagent such as nitric acid, which will react upon the different constituents of iron with different speed. The microphotographs are then taken of the resulting surfaces. Fig. 219 shows two typical microphotographs of this kind. This method of studying the structure of metals is known as *metallography* and is of great value.

## COMPOUNDS OF IRON

**The two series.** Iron differs from the metals so far studied in that it is able to form *two series* of compounds. In the one series the iron is *bivalent* and forms compounds which in formulas and many chemical properties are similar to the corresponding zinc compounds. These are called *ferrous* compounds. In the other series iron acts as a *tervalent* metal and forms salts similar to those of aluminum. These salts are known as *ferric* compounds. Iron is also present in a number of complex salts.

**Oxides of iron.** Iron forms several oxides. Ferrous oxide (FeO) is not found in nature but can be prepared artificially in the form of a black powder which easily takes up oxygen, forming ferric oxide:



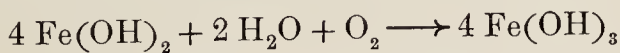
Ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) is the most abundant ore of iron and occurs in great deposits, especially in the Lake Superior region. It is found in many mineral varieties which vary in density

and color, the most abundant being *hematite*, which ranges in color from red to nearly black. When prepared artificially it is a bright-red powder which is used as a pigment (*Venetian red*) and as a polishing powder (*rouge*).

Magnetite has the formula  $\text{Fe}_3\text{O}_4$ . Its formula is sometimes written  $\text{Fe}(\text{FeO}_2)_2$ , indicating that magnetite is an iron salt of an acid also containing iron, but this is not certain. It is a very valuable ore, but is less abundant than hematite. It is sometimes called magnetic oxide of iron, or *loadstone*, since many specimens of it are natural magnets.

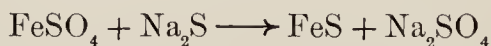
**Ferrous salts.** These salts are obtained by dissolving iron in the appropriate acid or, when they are insoluble, by precipitation. The crystallized salts are usually light-green in color and are hydrates. Ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ) is a base of about the same strength as the hydroxide of zinc or of magnesium. Consequently ferrous salts are not very much hydrolyzed in solution.

**Ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ).** This base forms as a white, nearly insoluble precipitate when a solution of a ferrous salt is treated with a soluble base. On exposure to the air and moisture it quickly oxidizes to a hydrated ferric oxide, generally written as  $\text{Fe}(\text{OH})_3$ :



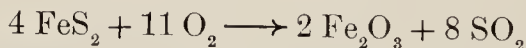
**Ferrous sulfate ( $\text{FeSO}_4$ ).** Ferrous sulfate is the most familiar ferrous compound. It is usually obtained in the form of the hydrate  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ , called *copperas* or *green vitriol*, and is prepared commercially as a by-product in the steel-plate mills. Preparatory to galvanizing or tinning (p. 485), steel plates are cleaned by immersing them in dilute sulfuric acid, and in the process some of the iron dissolves. The liquors are concentrated, and the green vitriol separates from them. The salt is used in the manufacture of ink and of iron alum, as a substitute for aluminum sulfate in the purification of water, and as a reagent to destroy weeds.

**Ferrous sulfide (FeS).** Ferrous sulfide is sometimes found in nature as a golden-yellow crystalline mineral called *pyrrhotite*. It is formed as a black precipitate when a soluble sulfide and an iron salt are brought together in solution :

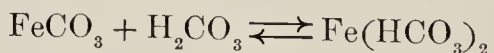


It can also be made as a heavy, dark-brown solid by fusing together the requisite quantities of sulfur and iron. It is used in the laboratory in the preparation of hydrogen sulfide (p. 280).

**Iron disulfide (pyrite) (FeS<sub>2</sub>).** This substance occurs abundantly in nature in the form of brass-yellow cubical crystals and in compact masses. Sometimes it is called *fool's gold* from its superficial resemblance to the precious metal. It is used in very large quantities as a source of sulfur dioxide in the manufacture of sulfuric acid, since it burns readily in the air, forming ferric oxide and sulfur dioxide :



**Ferrous carbonate (FeCO<sub>3</sub>).** This compound occurs in nature as *siderite* and is a valuable ore. Like calcium carbonate it dissolves to some extent in water containing carbon dioxide, forming the more soluble acid carbonate :

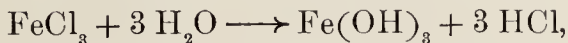


Spring waters containing acid carbonate in solution are called *chalybeate* waters.

**Ferric salts.** The crystallized ferric salts are usually yellow or violet in color. In solution and in the absence of free acid they hydrolyze even more readily than the salts of aluminum. This fact indicates that ferric hydroxide (Fe(OH)<sub>3</sub>) is a very weak base.

**Ferric hydroxide (Fe(OH)<sub>3</sub>).** When solutions of ferric salts are treated with ammonium hydroxide, a reddish-brown precipitate is obtained, which for convenience is given the formula Fe(OH)<sub>3</sub>. It is really a hydrated ferric oxide, of varying

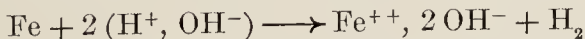
composition. It might be thought that this same precipitate would form when ferric salts undergo hydrolysis in solution,



but as a rule no precipitate forms, because the ferric hydroxide remains in colloidal dispersion. If the solution is boiled, some of this colloid is coagulated as a precipitate.

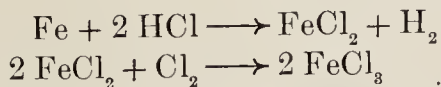
Iron *rust* is a variable mixture of hydrated oxides of iron. When a film of rust forms on iron, it does not protect the metal from the further action of water, as does the rust of aluminum and zinc, because iron rust is porous and also tends to scale off, exposing a fresh surface.

**The rusting of iron.** A number of different theories have been advanced to account for the changes taking place in the rusting of iron. The most satisfactory of these is known as the electrolytic theory. According to this the primary reaction in the rusting of iron is between iron and water, as expressed in the following equation:



The ions  $\text{Fe}^{++}$  and  $2 \text{OH}^-$  then combine to form ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ). This is further acted upon by oxygen and water, and forms the complex substance known as iron rust. It is evident that the composition of rust will vary according to the conditions of its formation.

**Ferric chloride ( $\text{FeCl}_3$ ).** This salt is the most familiar of the ferric salts. It can be obtained most conveniently by dissolving iron in hydrochloric acid and then passing chlorine into the solution:



The salt when crystallized from water is a reddish solid and has the formula  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ .

**Oxidation of ferrous salts.** A ferrous salt in solution, exposed to the action of the air or of an oxidizing reagent, is rapidly converted into a ferric salt by oxidation. For example, in the

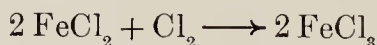


presence of hydrochloric acid the oxidation of ferrous chloride takes place, as follows:

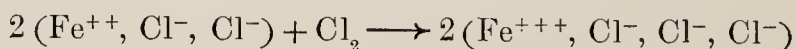


In the absence of free acid the reaction is somewhat more complicated but is of the same order.

It will be seen that the valence of the iron atoms has been increased from 2 to 3. *This increase in valence is always called oxidation*, even in cases in which no oxygen is concerned (p. 32), as is illustrated in the equation

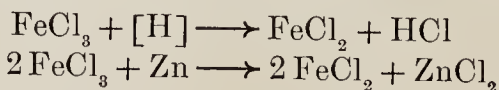


This equation may be written in such a way as to show the change in the electrical charges upon the ions:

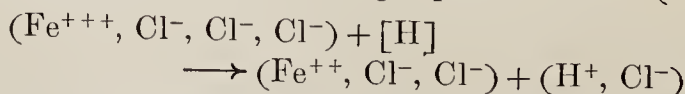


The charge upon each cation ( $\text{Fe}^{++}$ ) has been increased from 2 to 3, and a corresponding number of anions have been formed. In general, *the term oxidation is applied to all reactions in which the valence of a metallic cation is increased*. Much less frequently there are reactions in which the valence of the negative anion is diminished. This is also called oxidation.

**Reduction of ferric salts.** The changes that take place when a ferric salt is exposed to the action of nascent hydrogen or other reducing agents, such as metals, are the reverse of the ones just described. This is seen in the following equations:



In these reactions the valence of the iron atoms has been lowered from 3 to 2. These equations may also be written in a form to show the change of charge upon the cations ( $\text{Fe}^{+++}$ ):

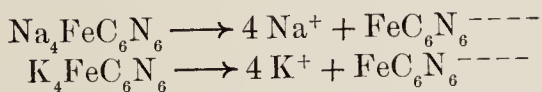


Although no oxygen has been removed, the ferric chloride is said to be *reduced*. In general, *when the valence of a metallic*

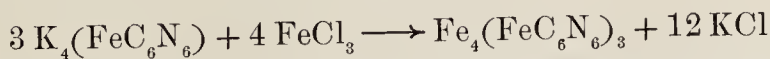
cation is diminished the salt is said to be reduced. Much less frequently there are reactions in which the valence of the negative anion is increased, and this is also called reduction.

**Sodium ferrocyanide ( $\text{Na}_4\text{FeC}_6\text{N}_6$ ); potassium ferrocyanide ( $\text{K}_4\text{FeC}_6\text{N}_6$ ).** These compounds are salts of the unstable ferrocyanic acid  $\text{H}_4\text{FeC}_6\text{N}_6$ . They are prepared from by-products obtained in the manufacture of coke. When the coal is heated in the absence of air, small quantities of the carbon, nitrogen, and hydrogen present are evolved in the form of hydrogen cyanide. This is absorbed and converted into calcium ferrocyanide by means of calcium hydroxide and the spent iron oxide employed in the purification of the gas evolved in the coking of the coal. The calcium ferrocyanide so obtained is converted into sodium or potassium ferrocyanide by treatment with appropriate salts of sodium or potassium. The reactions involved in the complete process are quite complex.

Both sodium ferrocyanide and potassium ferrocyanide are yellow in color and are readily soluble in water. The latter compound is often called *yellow prussiate of potash*. The sodium salt crystallizes from water in the form of the hydrate  $\text{Na}_4\text{FeC}_6\text{N}_6 \cdot 10 \text{H}_2\text{O}$ , while the potassium salt crystallizes as the hydrate of  $\text{K}_4\text{FeC}_6\text{N}_6 \cdot 3 \text{H}_2\text{O}$ . In solution they ionize as follows:

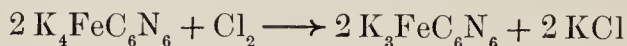


It is important to notice that no ions of iron are present, so that these salts do not give the ordinary reactions for iron. They react with ferric salts such as ferric chloride in accordance with the following equation:



The resulting ferric ferrocyanide is a blue, insoluble solid and is ordinarily called *Prussian blue*. It is a common paint pigment, and most of the ferrocyanides made are used in the preparation of this pigment.

**Potassium ferricyanide ( $K_3FeC_6N_6$ ).** By treating a solution of potassium ferrocyanide with chlorine water and evaporating the solution to crystallization, garnet-red crystals are deposited which have the composition  $K_3FeC_6N_6$ :



This compound is called potassium ferricyanide, or *red prussiate of potash*. It will be noticed that in this reaction the composition of the anion is not changed, but its charge is diminished. The reaction is therefore an oxidation of the ferrocyanide. In place of chlorine one may use nascent oxygen evolved by electrolysis. It is only necessary to electrolyze a solution of potassium ferrocyanide in water. The oxygen evolved at the anode converts the potassium ferrocyanide into the ferricyanide.

**Blue-printing.** When a ferric salt and potassium ferricyanide are brought together in solution, no precipitate forms, though the solution acquires a yellowish color. On exposure to the sunlight the ferric salt undergoes a partial reduction to a ferrous salt, and a blue precipitate forms. Advantage is taken of these facts in the process of *blue-printing*. A sensitive paper is prepared by soaking paper in a solution of potassium ferricyanide and a ferric salt (ferric ammonium citrate is generally used) and drying it in a dark place. When a black drawing on tracing cloth is placed upon such a sensitive paper and the two are exposed to the sunlight, the sensitive paper (except where it is protected by the black lines) turns a brownish color. It is then thoroughly washed with water to remove the soluble salts, during which process the portions acted upon by the light turn blue, while the unaffected portions are left white. A solution of sodium hydroxide can be used as an ink for white lettering on a blue print, since this base decolorizes Prussian blue.

**Other salts of iron.** The following compounds of iron have industrial uses:

Ferric sulfate ( $Fe_2(SO_4)_3$ ) . . . . .	a white solid
Ferric nitrate ( $Fe(NO_3)_3 \cdot 6 H_2O$ ) . . . . .	violet crystals
Iron alum ( $NH_4Fe(SO_4)_2 \cdot 12 H_2O$ ) . . . . .	violet crystals

**Reactions for distinguishing between ferrous and ferric salts.** One of the most sensitive methods for distinguishing between ferrous and ferric salts is the reaction with ammonium sulfocyanate ( $\text{NH}_4\text{CNS}$ ). A solution of this salt gives no color whatever when added to a solution of a ferrous salt; but with ferric salts it gives a deep red color due to the formation of the red ferric sulfocyanate ( $\text{Fe}(\text{CNS})_3$ ). Similarly, potassium ferrocyanide added to a solution of a ferrous salt gives a bluish-white color, while with ferric salts Prussian blue is formed.

### INKS

**Composition.** Inks were known as early as 2500 B.C. and were used in writing. They were black and, like modern india ink, owed their color to carbon. The composition of ordinary black ink may be seen from the following formula, recommended by the United States government: tannic acid, 23.4 g.; gallic acid, 7.7 g.; ferrous sulfate, 30 g.; dilute hydrochloric acid, 25 g.; carbolic acid (phenol), 1 g.; suitable blue dye, 2.2 g.; sufficient water to make 1000 cc.

Tannic acid and the closely related compound gallic acid are obtained from the bark of various trees and especially from nut-galls (abnormal growths produced on parts of trees that have been stung by certain insects). *Ferrous salts* do not form a color with tannic and gallic acids, but *ferric salts* produce a black tannate and gallate of iron. When the ink is used, the ferrous salt is oxidized by the air to a ferric salt, and this then forms the black iron compound. The dye called for in the formula is used to give a temporary color until the permanent color develops. The acid is necessary to keep the iron in solution. The carbolic acid acts as a preservative to keep the ink from molding. *Circular No. 95*, issued by the United States Bureau of Standards, gives interesting information concerning inks.

### COBALT AND NICKEL

**Occurrence.** Cobalt and nickel are almost always found together in ores which also contain iron, silver, and copper, in combination with arsenic and sulfur. The richest deposits of cobalt are located at Cobalt (Ontario), while the chief mines of nickel are at Sudbury (Ontario) and the French



Island of New Caledonia. The mines at Cobalt are also rich in silver. The extraction of these metals from their ores and their separation from each other is too complicated a process to be described here. Nickel is also a frequent impurity of crude copper, and several million pounds of nickel sulfate are annually recovered in the United States in the refining of copper by electrolysis.

**Properties and uses.** Both these metals are silvery in appearance and take a high polish. They are somewhat heavier than iron, and melt at a lower temperature. Their chief use is in making alloys. The alloy known as *stellite* consists chiefly of cobalt and chromium and is used for making cutlery. Its chief advantage is that it does not rust. Cobalt steels retain their temper at high temperatures and are useful for making high-speed cutting tools. Nickel coinage used in the United States consists of 75 per cent of copper and 25 per cent of nickel. Some coins used in Canada are made of pure nickel. German silver (p. 552) also contains about 25 per cent of nickel. Nickel steel usually contains about 3.5 per cent of nickel, and prior to the war more than half of the nickel produced was used in making this product, largely for the manufacture of armor plate. The partial scrapping of the navies has greatly diminished the demand for nickel, but nickel steels containing various percentages of nickel are in demand for many purposes, such as the construction of machinery, automobiles, and locomotives. *Invar* contains about 36 per cent of nickel and does not expand when heated. *Monel metal* is an alloy consisting of 67 per cent of nickel, 28 per cent of copper, and 5 per cent of iron. It possesses very great tensile strength, is tough and ductile, and does not corrode, so that it finds many uses. Modern rifle bullets are made of an alloy of copper and nickel of about the composition of Monel metal. They are as hard as steel and much heavier. Nickel is extensively used as a plating upon other metals, such as iron or brass, to prevent tarnishing in air, and cobalt can be used in the same way.

Finely divided nickel is used as a catalyzer in a number of reactions, such as the conversion of oils into solid fats (p. 417).

**Electroplating with nickel.** Nickel plating is accomplished by an electrolytic process. The electrolyte consists of a solution of nickel ammonium sulfate, a salt having the composition  $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ . The object to be plated is suspended in the electrolyte and serves as the cathode, while a plate of nickel

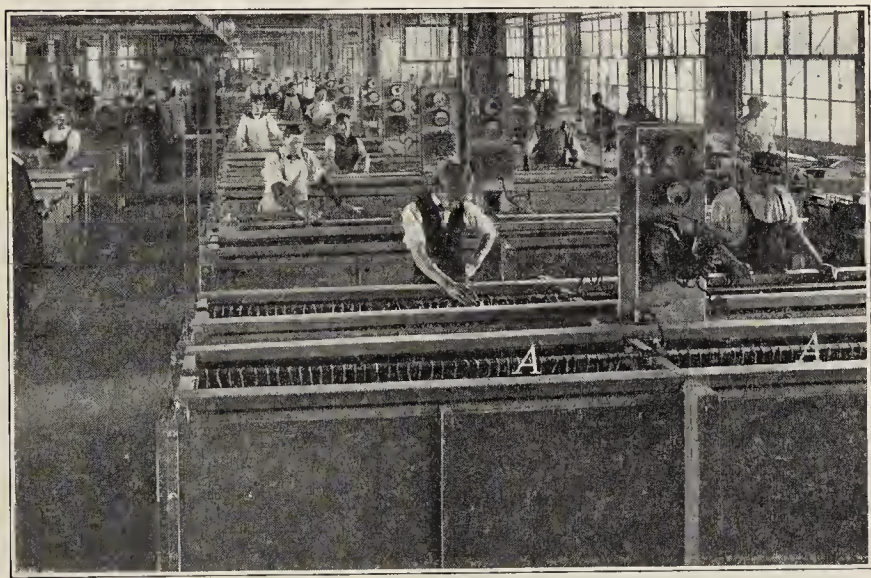


FIG. 220. A view in a factory showing the process of nickel plating  
The objects to be plated are suspended in a bath of the nickel salt in such a way  
that they form the cathode

is used as the anode. When the current is passed through the electrolyte, the nickel is deposited upon the object to be plated, and an equivalent portion of nickel dissolves from the anode, the composition of the electrolyte remaining unchanged. Fig. 220 illustrates the process carried out on a large scale, the objects to be plated being suspended from the rods *A*, *A*.

**Cobalt oxide ( $\text{CoO}$ ).** This is the form in which most of the cobalt comes into the market. It is a black powder used in making other cobalt compounds and in making blue glass and blue decorations on china. Sometimes ground blue cobalt glass, called *smalt*, is used instead of the oxide and as a pigment.

**Salts of cobalt and nickel.** Nearly all the simple salts of cobalt and of nickel have formulas similar to those of *ferrous* salts. The most familiar are the following:

$\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ . . . . .	a cherry-red deliquescent salt
$\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ . . . . .	similar in appearance to the nitrate
$\text{CoS}$ . . . . .	an insoluble black solid
$\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ . . . . .	well-formed green crystals
$\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ . . . . .	deliquescent green crystals
$\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$ . .	used in nickel plating
$\text{NiS}$ . . . . .	an insoluble black solid
$\text{Ni}(\text{CO})_4$ (nickel carbonyl) . . .	colorless liquid boiling at $43.2^\circ$

### EXERCISES

1. In the manufacture of cast iron, why is the air heated before being forced into the furnace?

2. Write the equations showing how each of the following compounds of iron could be obtained from the metal itself: ferrous chloride, ferrous hydroxide, ferrous sulfate, ferrous sulfide, ferrous carbonate, ferric chloride, ferric sulfate, ferric hydroxide.

3. Account for the fact that a solution of sodium carbonate, when added to a solution of a ferric salt, precipitates a hydroxide and not a carbonate.

4. How could you prepare ferric chloride from copperas?

5. Why is brass often nickel plated?

6. Why does not iron occur in the native state? What does its native occurrence in meteorites indicate?

7. Why is the furnace in which cast iron is made called a blast furnace?

8. Write equations for the oxidation of ferrous sulfate to ferric sulfate; for the reduction of ferric sulfate to ferrous sulfate.

9. Suggest a method for removing the iron from chalybeate waters.

10. Why is the formula for Prussian blue written  $\text{Fe}_4(\text{FeC}_6\text{N}_6)_3$  rather than  $\text{Fe}_7(\text{C}_6\text{N}_6)_3$ ?

11. Will ammonium hydroxide precipitate ferric hydroxide when added to a solution of sodium ferrocyanide?

12. Explain how it is possible to use the compounds of iron  $\text{K}_4\text{Fe}(\text{CN})_6$  and  $\text{K}_3\text{Fe}(\text{CN})_6$  in testing for the presence of iron in compounds.

**13.** Should you expect a solution of ferrous sulfate to react acid, basic, or neutral?

**14.** Write the equation for the reaction that takes place when pyrite is roasted in the air to obtain sulfur dioxide used in the manufacture of sulfuric acid.

**15.** Suppose you wished to reduce ferric chloride to ferrous chloride, how can you tell when the reduction is complete?

**16.** Which of the ores of iron are richest in iron?

**17.** The iron ore from a certain mine is hematite, 90 per cent pure. Approximately what weight of steel containing 1 per cent of carbon can be prepared from 1000 tons of this ore, assuming that 10 per cent of iron is lost in the process?

**18.** A sulfuric-acid plant has a daily output of 100 tons of acid containing 50 per cent of hydrogen sulfate. What weight of pyrite is required daily to furnish the necessary sulfur dioxide, assuming that the ore is 95 per cent pure and that 5 per cent of the sulfur is lost in the process?

**19.** What weight of pyrite is necessary for the preparation of 1000 kg. of Venetian red?

**20.** What weight of potassium ferricyanide will 10 kg. of crystalline potassium ferrocyanide yield?



## CHAPTER XL

### COPPER; MERCURY; SILVER

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	FORMULAS OF OXIDES	
					-ous	-ic
Copper . . . . .	Cu	63.57	8.9	1083.00°	Cu <sub>2</sub> O	CuO
Mercury . . . . .	Hg	200.61	13.5	- 38.87°	Hg <sub>2</sub> O	HgO
Silver . . . . .	Ag	107.880	10.5	960.50°	Ag <sub>2</sub> O	

**General.** Although these three elements do not form a periodic family (copper and silver belonging to one family and mercury to another), they have much in common, and it is convenient to describe them together. They are the first metals to be described that fall below hydrogen in the electrochemical series and do not liberate hydrogen from acids and water. They differ from the other metals already described in that they are found free in nature. Silver is univalent and forms but one series of salts. Copper and mercury form two series of salts, in which the metals are univalent and bivalent respectively.

### COPPER

**Occurrence.** Metallic copper has been known from the earliest times and was probably the first metal to come into any considerable use. This is explained by the fact that it occurs native and is easily hammered into desired shapes. It owes its name (from the Latin word *cuprum*) to the fact that the Romans obtained it from the island of Cyprus.

Large quantities of native copper, in a state approximating purity, are found in the northern peninsula of Michigan. Smaller deposits are also found in a number of other localities. In combination it is found in a wide variety of forms, especially as sulfides, oxides, carbonates, and silicates. In small quantities it is present in the great majority of sulfide minerals, and in traces it is very widely distributed in nature. To some extent it is absorbed by plants growing in copper-bearing regions, and it is also assimilated by some animals. It is present in certain forms of marine life; thus, oysters always contain it, sometimes in sufficient quantities to give a green color to them.

**Ores of copper.** The table which follows gives a list of the most important ores, chalcopyrite being by far the most valuable. Much copper is also produced from impure native copper.

SULFUR ORES	OXYGEN ORES
Chalcopyrite . . . . . $\text{CuFeS}_2$	Cuprite . . . . . $\text{Cu}_2\text{O}$
Chalcocite . . . . . $\text{Cu}_2\text{S}$	Melaconite . . . $\text{CuO}$
Bornite . . . . . $\text{Cu}_5\text{FeS}_4$	Malachite . . . . $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$

The most important copper-producing regions in the United States are Arizona, Montana (Fig. 221), Utah, and Michigan. Nearly all civilized countries produce some copper, but the United States produces more than half of the world's supply. Enormous deposits have been opened up in Chile that promise in time to make that country the leading copper-producing nation of the world. The world's production varies considerably from year to year, but the normal output is about 1,000,000 tons annually.

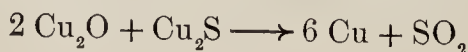
**Metallurgy.** The metallurgy of copper is so complex that only a brief statement of the principles involved will be given. Two general methods are in use: (1) In the *leaching method*, of limited application, the ore is treated with some liquid, such as sulfuric acid or ammonium hydroxide, that will

dissolve out the copper. (2) The *smelting method* is more generally applicable. In this method the copper ore used is in the form of a sulfide mixed or combined with other metallic sulfides, especially iron, as well as with small percentages of gold and silver. The ore is heated with an appropriate flux in a blast furnace or a reverberatory furnace. The sulfides of copper and iron melt, and the resulting liquid (known as *matte*)



FIG. 221. View in a copper mine at Butte, Montana

is separated from the slag and run into specially designed Bessemer converters. Any gold and silver present in the original ore is in solution in the liquid matte. Silica is now added, and air is forced through the converter. The sulfides are changed to oxides by the process. The iron oxide combines with the silica, forming a slag that can be poured off, while the copper oxide reacts with some unchanged copper sulfide as follows:





The resulting copper, which contains any gold or silver present in the ore, is run into molds and in this form is known as *blister copper*. This generally contains about 3 per cent of impurities and is refined by electrolysis.

**Refining of copper.** Many of the purposes for which copper is used require a very pure metal, and for these purposes blister copper must be refined. This is accomplished by electrolysis.

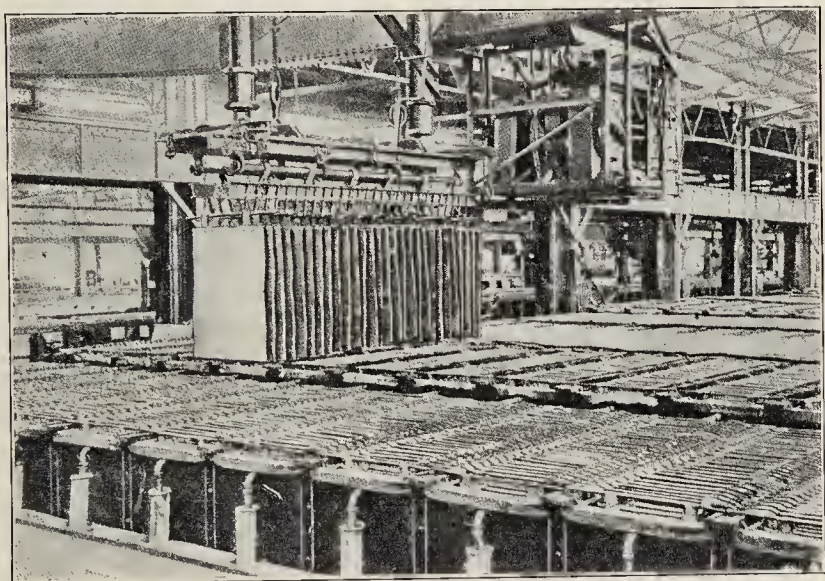


FIG. 222. View in an electrolytic copper refinery: withdrawing the pure copper cathodes from the cells

**Electrolytic refining.** The copper from the converter is cast into anode plates weighing upwards of 300 pounds. These are suspended in tanks (Fig. 222) containing a solution of copper sulfate as electrolyte, each anode plate being arranged opposite to a cathode made of a thin sheet of pure copper. The current, in passing through the cell, dissolves copper from the anode and deposits it upon the cathode in very pure form, the insoluble impurities collecting on the bottom of the tank as a mud. The cathode copper, while pure, is porous and is melted and cast into compact ingots. The electrolytic mud contains the gold and silver which was in the blister copper and is worked over for these metals.



**Flotation method for concentrating ores.** This method is a novel one recently introduced for concentrating ores, especially sulfide ores, not only of copper but of other metals as well. The ore is very finely pulverized and run into large tanks. Water, together with a small quantity of pine oil (or some similar oil), is added to the ore and thoroughly mixed through it, either by stirring devices or by forcing compressed air through the mass. The oil, or the froth formed by blowing the air through the liquid, forms an envelope about the ore particles but not about the impurities. The froth rises to the surface of the water, carrying the particles of ore, which can then be separated.

**Properties of copper.** Copper is a rather heavy metal, of density 8.9, and has a characteristic reddish color. It is rather soft and is very malleable, ductile, and flexible, yet tough and strong. As a conductor of heat and electrical energy for a given cross section of wire it is second only to silver.

Since it is below hydrogen in the electrochemical series, hydrochloric acid, dilute sulfuric acid, and fused alkalies are almost without action upon it; nitric acid and hot concentrated sulfuric acid, however, readily dissolve it (pp. 232, 294). In moist air it slowly becomes covered with a film of the bright-red oxide  $\text{Cu}_2\text{O}$ , which soon changes to a green basic carbonate. Heated in the air, the metal is oxidized to  $\text{CuO}$ .

**Uses.** About one fourth of all the copper produced is used for electrical purposes. The remainder is used for various purposes, such as for making wire and automobiles, for sheathing the bottoms of ships, and for making alloys. In the following table the composition of some of these alloys is indicated:

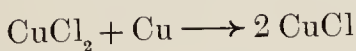
Aluminum bronze . . . . .	90%-98% copper, 2%-10% aluminum
Brass . . . . .	63%-73% copper, 27%-37% zinc
Bronze . . . . .	70%-95% copper, 1%-25% zinc, 1%-18% tin
German silver . . . . .	50%-60% copper, 20% zinc, 20%-30% nickel
Gun metal . . . . .	90% copper, 10% tin
Gold coin . . . . .	10% copper, 90% gold
Silver coin . . . . .	10% copper, 90% silver
Nickel coin . . . . .	75% copper, 25% nickel

**Electrotyping.** Books are often printed from electrotype plates, which are prepared as follows: The face of the type is covered with wax, and this is firmly pressed down until a clear impression is obtained. The impressed side of the wax is coated with graphite, and this is made the cathode in an electrolytic cell containing a copper salt in solution. The copper is deposited as a thin sheet upon the letters in wax and, when detached, is a perfect copy of the type, the under part of the letters being hollow. The sheet is strengthened by pouring on the undersurface a suitable amount of commercial lead. The sheet so strengthened is then used in printing.

**Two series of copper compounds.** Copper, like iron, forms *two series* of compounds: the *cuprous* compounds, in which it is univalent; and the *cupric* compounds, in which it is bivalent. The cupric salts are much the more common of the two.

**Cuprous compounds.** The most important cuprous compound is the oxide,  $\text{Cu}_2\text{O}$ , which occurs in nature as *ruby copper*, or *cuprite*. It is a bright-red substance and can easily be prepared by heating copper to a high temperature in a limited supply of air. It is used for imparting a ruby color to glass. By treating cuprous oxide with different acids a number of cuprous salts can be made.

Cuprous chloride ( $\text{CuCl}$ ) is the best-known cuprous salt. It can be made by boiling a solution of cupric chloride with copper:

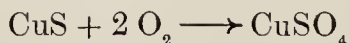


It is a white salt, nearly insoluble in water. It dissolves readily in ammonia water, and the resulting solution is a solvent for many gases, especially carbon monoxide and acetylene.

**Cupric compounds.** Cupric salts are easily made by dissolving cupric oxide in acids or, when insoluble, by precipitation. In crystallized form most of them are blue or green. Since they are so much more familiar than the cuprous salts, they are frequently called merely copper salts.

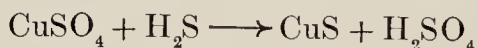
**Cupric oxide ( $\text{CuO}$ ).** This is a black insoluble substance obtained by heating copper in excess of air or by igniting the hydroxide or the nitrate. It is used as an oxidizing agent.

**Cupric sulfate ( $\text{CuSO}_4$ ).** When crystallized from water, cupric sulfate forms large blue crystals of the hydrate  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ , called *blue vitriol* or *bluestone*. The salt is a by-product in silver refining and is also made by the oxidation of pyrite containing copper:



The salt finds extensive use in electrotyping, in copper refining, as a remedy for hoof diseases (particularly in sheep), and in the manufacture of insecticides. Like all copper salts, it is poisonous, especially to lower forms of life. When it is added, even in very minute quantities, to water containing green pond scum (algæ), the plant is quickly killed. Mixed with calcium hydroxide and water it forms a complex mixture known as *Bordeaux mixture*, which is used as a spray for killing molds and scale on fruit trees and vegetables.

**Cupric sulfide ( $\text{CuS}$ ).** In the form of a black insoluble precipitate, cupric sulfide ( $\text{CuS}$ ) is easily prepared by the action of hydrogen sulfide upon a solution of a copper salt:



It is insoluble in water and in dilute acids.

**Other cupric salts.** Among the other cupric salts frequently used in the laboratory are the following, most of which form other hydrates in addition to those given:

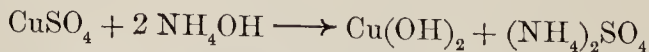
Cupric nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ ): blue deliquescent crystals

Cupric chloride ( $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ ): light-blue, pearly scales or needles

Cupric bromide ( $\text{CuBr}_2$ ): brownish-purple crystals resembling iodine

Cupric acetate ( $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ ): a blue, easily crystallized salt

**Cupric ammonia compounds.** When cupric sulfate in solution is treated with aqua ammonia, the insoluble hydroxide is at first precipitated:



Continued addition of ammonia causes the precipitate to dissolve, forming an intensely colored blue-purple solution. When alcohol is added to the solution, a colored salt crystallizes, which is found to have the formula  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ . In solution this salt does

not give simple cupric ions ( $\text{Cu}^{++}$ ), but the cation is  $\text{Cu}(\text{NH}_3)_4^{++}$  and the anion is  $\text{SO}_4^{--}$ . All soluble copper salts give a solution of this same blue-purple color when treated with an excess of ammonia, and all these solutions contain the complex cation  $\text{Cu}(\text{NH}_3)_4^{++}$ . The anion may be any acid radical, so that we have such salts as the following:  $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$ ;  $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$ ;  $\text{Cu}(\text{NH}_3)_4\text{CO}_3$ . Many other metals form similar salts, especially cobalt, nickel, and platinum, and these are sometimes called *ammino salts*.

**Electric cells.** An electric cell is a device for converting chemical energy directly into electrical energy instead of into heat. A great many different chemical reactions can be arranged in such a way as to accomplish this result, and the combination known as the Daniell cell will serve as an illustration of the most familiar types of cells. In this combination two plates, one of copper and the other of zinc, each fashioned so as to have a large surface, are arranged in a glass jar, as shown in Fig. 223. The electrolyte in contact with the zinc plate is zinc sulfate, while that in contact with the copper plate is copper sulfate.

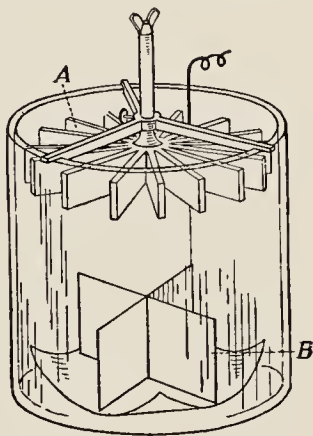


FIG. 223. A simple type of electric cell, called the Daniell cell

**Chemical reactions in a cell.** The action of the cell can be explained as follows: The zinc atoms of the plate A have a tendency to leave the plate and to pass into solution as zinc ions. But since each zinc ion ( $\text{Zn}^{++}$ ) carries two positive charges, the formation of each of these ions leaves the plate negatively charged with two electrons. The accumulation of this charge (electrons) soon prevents the formation of more zinc ions, and the process stops in an equilibrium.

On the other hand, copper ions ( $\text{Cu}^{++}$ ) from the dissolved copper sulfate have a tendency to deposit upon the copper plate B as metallic atoms, each copper ion bringing to the plate two positive



charges. The accumulation of these charges on the plate soon prevents the deposit of more copper ions, and equilibrium results.

If now the two plates are joined by an electrical conductor (a metal wire), the negative charge (excess electrons) on the zinc plate neutralizes the positive charge on the copper plate by flowing through the wire. The solution of the zinc and the deposit of the copper can now proceed as long as the two plates are connected. The chemical reaction taking place is represented by the equation :



In this particular reaction all the heat can be converted into electrical energy, which may be obtained from the wire and may in turn be converted into work.

The order of the metals in the electrochemical series (p. 216) is the order of intensity with which the metals tend to pass into ionic form. *Any two metals in a suitable electrolyte will constitute a cell in which the metal higher in the series is the negative pole and the lower one the positive.* As a rule, only a part of the chemical energy is converted into electrical energy, the remainder being transformed into heat.

## MERCURY

**Occurrence.** Mercury is familiar to all as the *quicksilver* used in thermometers and barometers. It has long been known and was highly esteemed by the alchemists, who regarded it as a component of all the metals. It is the only metal which is liquid at ordinary temperatures. Mercury occurs in nature chiefly as the sulfide  $\text{HgS}$ , called *cinnabar*. The mercury mines of Spain have long been famous. At present Italy is the chief producer of mercury, followed by Spain, California, and Texas. It comes on the market in iron flasks; each flask contains about 75 lb. About 100,000 flasks of mercury are produced annually.

**Metallurgy.** Mercury is a volatile metal which has but little affinity for oxygen, and this makes the metallurgy of mercury very simple. The crushed ore, mixed with a small quantity of carbon to reduce any oxide or sulfate that might be formed, is roasted in a current of air. The sulfur burns to sulfur dioxide,

while the mercury vaporizes and is condensed in a series of condensing vessels. The metal is purified by distillation.

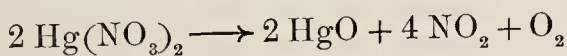
**Properties.** Mercury is a heavy, silvery liquid whose density is 13.546. It boils at  $356.9^{\circ}$  and solidifies at  $-38.87^{\circ}$ . It forms alloys (called *amalgams*) with nearly all metals.

Toward acids mercury conducts itself very much like copper; it is easily attacked by nitric acid and by hot concentrated sulfuric acid, while cold sulfuric acid and hydrochloric acid have no effect on it.

**Uses.** Mercury is extensively used in the construction of many scientific instruments, such as the thermometer and the barometer, and as a liquid over which to collect gases that are soluble in water. The readiness with which it alloys with silver and gold makes it very useful in the extraction of these elements. All salts of mercury are made directly or indirectly from the purified metal.

**Compounds of mercury.** Like copper, mercury forms two series of compounds: the *mercurous* compounds, of which mercurous chloride ( $\text{HgCl}$ ) is an example; and the *mercuric* compounds, represented by mercuric chloride ( $\text{HgCl}_2$ ).

**Mercuric oxide ( $\text{HgO}$ ).** Mercuric oxide is usually obtained as a brick-red substance by carefully heating the nitrate:



It can also be obtained in a yellow form by adding a cold solution of potassium hydroxide to a solution of a mercuric salt. The hydroxide which would be expected to form in the reaction spontaneously decomposes into the oxide:

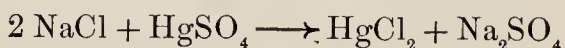


When heated the oxide becomes almost black; at a higher temperature it decomposes into mercury and oxygen (p. 28).

**Mercuric sulfate ( $\text{HgSO}_4$ ).** This salt is easily prepared by the action of an excess of concentrated sulfuric acid upon mercury, the reaction being like that of the acid upon copper

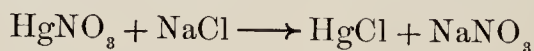
(p. 294). It is a white solid, soluble in dilute sulfuric acid but hydrolyzed into a yellow basic salt by pure water.

**Mercuric chloride (corrosive sublimate) ( $\text{HgCl}_2$ ).** This compound can be made by dissolving mercuric oxide in hydrochloric acid. On a commercial scale it is made by heating a mixture of common salt and mercuric sulfate:



The mercuric chloride, being readily volatile, vaporizes and is condensed again in cool vessels. It is a white solid and is soluble in water. It is extremely poisonous and in dilute solutions is used as an antiseptic in dressing wounds.

**Mercurous chloride (calomel) ( $\text{HgCl}$ ).** Being insoluble, mercurous chloride is precipitated as a white solid when a soluble chloride is added to a solution of mercurous nitrate:



Commercially it is manufactured by heating a mixture of mercuric chloride and mercury. It is a common medicine.

**Mercuric sulfide ( $\text{HgS}$ ).** This compound occurs in nature as a red solid (cinnabar, p. 556). By passing hydrogen sulfide into a solution of mercuric salt, mercuric sulfide is precipitated as a *black* powder insoluble in water and acids. By other means it can be prepared as a brilliant red powder, known as *vermilion*, which is used as a pigment in fine paints.

**Other salts of mercury.** The following salts have frequent uses in the laboratory:

Mercurous nitrate ( $\text{HgNO}_3 \cdot 2 \text{H}_2\text{O}$ ): colorless crystals soluble in dilute nitric acid

Mercuric nitrate ( $\text{Hg}(\text{NO}_3)_2 \cdot 8 \text{H}_2\text{O}$ ): colorless crystals soluble in dilute nitric acid

Mercurous sulfate ( $\text{Hg}_2\text{SO}_4$ ): a white crystalline solid nearly insoluble in dilute acids

Mercuric fulminate ( $\text{Hg}(\text{ONC})_2$ ): a white solid made by the action of nitric acid upon mercury in the presence of alcohol. It is used as the explosive material in percussion primers

## SILVER

**History and occurrence.** The fact that silver occurs native, and that it has a bright, permanent luster, led to the early use and appreciation of this metal. Mention is made of it as far back as 4500 B.C. It was highly prized by the ancients and was used then, as now, as a medium of exchange and for ornaments. The Greeks called it *argyros*, and the Romans, *argentum*. The alchemists refer to it under the name of *luna* (the moon's metal), and silver nitrate, even now, bears the common name *lunar caustic*.

While silver occurs native, and instances are recorded in which masses weighing as much as 100 lb. each have been found, nevertheless the metal is usually found in combination with sulfur, either as the sulfide  $\text{Ag}_2\text{S}$  or as a constituent of other sulfides, especially those of lead, copper, antimony, cobalt, and arsenic. It is found in small quantities in nearly all copper and lead ores, and much of our supply comes from this source.

**The refining of silver.** In the United States silver is produced almost entirely in connection with lead, and it will be convenient to consider the metallurgy of these two metals together in the next chapter. The crude silver produced by any process may contain a number of metals, especially copper and gold, and is usually refined either by *parting* with sulfuric acid or by electrolysis.

1. **Cupellation and parting with sulfuric acid.** In this process the impure metal is heated on an open hearth in a strong current of air. The various metallic impurities (excepting gold) are in this way largely converted into oxides and swept off as dross, leaving the silver alloyed with small percentages of gold, copper, and iron. It is then cast into ingots known as *doré* bars, since they contain gold.

In order to recover the gold the alloy is treated with hot concentrated sulfuric acid, which converts into sulfates all the metals except the gold. When water is added to the resulting



mixture the sulfates of copper, silver, and iron pass into solution, while the gold, together with the lead sulfate and any unattacked substances, settles as a mud from which the gold is subsequently recovered. The silver is separated from the solution of the sulfates by suspending in it clean copper plates, the copper displacing the silver, which is deposited in crystalline form:



The copper sulfate obtained as a by-product in this process furnishes much of the blue vitriol of commerce.

**2. *Electrolytic refining.*** Electrolysis of the impure silver is now carried out extensively, the process being conducted in a way very similar to the electrolysis of copper. The electrolyte used is a solution of silver nitrate in nitric acid. The silver is deposited as crystals, which are mechanically brushed off the cathode, collected, and melted into bars.

**Production.** For a number of years the world's annual production of silver has averaged about 5,500,000 kg. The United States produces a little more than one third of this amount, and Mexico about an equal percentage. In the United States the chief silver-producing states are Utah, Montana, Nevada, and Idaho.

**Properties of silver.** Silver is a heavy, rather soft, white metal, very ductile and malleable, and capable of taking a high polish. It melts at  $960.5^\circ$ , boils at  $1950^\circ$ , and has a density of 10.5. It surpasses all other metals as a conductor of heat and electricity, but is too costly to find extensive use for such purposes. It melts at a little lower temperature than copper. It alloys readily with other heavy metals, and when it is to be used for coinage or for tableware a small quantity of copper—from 8 per cent to 10 per cent—is melted with it to give it hardness (sterling silver).

It is not acted upon by water or air but is quickly tarnished when in contact with sulfur compounds (eggs, mustard, perspiration), turning quite black in time. Hydrochloric acid

and fused alkalis do not act upon it, but nitric acid and hot concentrated sulfuric acid dissolve it with ease. When a solution of a silver salt is treated with a strong reducing agent, metallic silver is precipitated. Under proper conditions this takes the form of a brilliant mirror deposited on the sides of the glass vessel. *Mirrors* and glass reflectors are usually made in this way.

**Electroplating with silver.** Since silver is not acted upon by water or air, and since it has a pleasing appearance, it is used to coat various articles made of cheaper metals. Such articles are said to be *silver plated*, and the process by which this is done is very similar to electroplating nickel (p. 545). The object to be plated (as, for example, a spoon) is attached to a wire and dipped into a solution of a suitable silver salt. Electrical connection is made in such a way that the article to be plated is the cathode (Fig. 224), while the anode *A* is made up of one or more plates of silver.

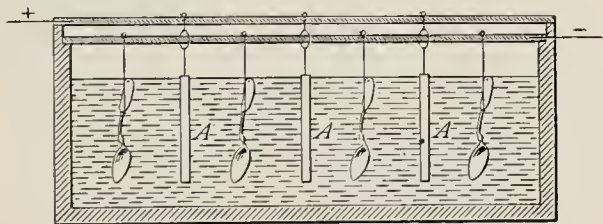


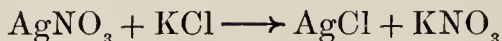
FIG. 224. The process of plating

**Compounds of silver.** Silver forms only one well-defined series of salts, which corresponds to the mercurous and the cuprous series.

**Silver nitrate (lunar caustic) ( $\text{AgNO}_3$ ).** This salt is easily prepared by dissolving silver in nitric acid and evaporating the resulting solution. It crystallizes in flat, colorless plates, and when heated carefully can be melted without decomposition. When cast into sticks it is called *lunar caustic*, for it has a very corrosive action on flesh and is sometimes used in surgery to burn away abnormal growths.

**Compounds of silver with the halogens.** The chloride, the bromide, and the iodide of silver (often termed collectively the *silver halides*) are insoluble in water and in acids and therefore

are precipitated by bringing together a soluble halogen salt with silver nitrate:



They form amorphous, curdy precipitates, the chloride being white, the bromide very pale yellow, the iodide decidedly yellow. They are remarkable for the fact that they are very sensitive to the action of light, undergoing a change of color and chemical composition when exposed to sunlight, especially if in contact with organic matter, such as gelatin. It is upon this property of the silver halides that the art of photography is based.

**Some less important salts.** The following is a list of some of the silver salts used in the arts or in analysis:

Silver sulfate ( $\text{Ag}_2\text{SO}_4$ ): a sparingly soluble salt crystallizing in white needles

Silver nitrite ( $\text{AgNO}_2$ ): a white salt soluble in hot water

Silver sulfide ( $\text{Ag}_2\text{S}$ ): found in nature as *argentite*. It is insoluble both in water and in acids and may be prepared by precipitation as a black powder

Silver cyanide ( $\text{AgCN}$ ): a curdy white precipitate insoluble in water

Silver chromate ( $\text{Ag}_2\text{CrO}_4$ ): a brick-red solid prepared by precipitation

**Uses.** The principal use of silver is for coinage. The standard silver coin used in the United States is made of an alloy of 10 per cent copper and 90 per cent silver. The many other uses of silver are well known to all. It is interesting to note the increasing amount used in photography; about 5,000,000 oz. is used annually for this purpose. At present the "movie" films made annually, if placed end to end, would encircle the earth about five times.

## PHOTOGRAPHY

**The sensitive plate or film.** The silver halides become super-sensitive to light when in the colloidal state in the presence of a protecting colloid such as gelatin or collodion. Such a suspension is termed a photographic emulsion. These may consist of a dispersion of either silver chloride, bromide, or iodide, or a mixture

of these. A gelatin emulsion is prepared by adding to the liquid gelatin the corresponding halides of sodium or potassium and then adding a solution of silver nitrate slowly and with constant stirring. The resulting milky emulsion is then cooled, when it sets to a stiff jelly, which in turn is shredded and washed to

remove the free potassium nitrate. The shredded emulsion is then melted and coated in a thin layer on a suitable support, which may be either glass, paper, or film, composed of nitrocellulose or cellulose acetate (p. 398).



FIG. 225. The negative plate, or film

film so prepared is placed in a camera and the image of some object is impressed upon it, the particles of silver halide in the emulsion undergo a change (not well understood) which is proportional to the intensity of the light falling upon it. In this way an image of the object photographed is produced upon the plate. The image, however, is invisible and is therefore called *latent*. It can be made visible by the process of *development*.

**Developing the latent image.** When the exposed emulsion is placed in a suitable developing solution, the exposed grains of silver halide are reduced to metallic silver, while the unexposed grains remain unaffected. The developer usually consists of a mixture of an organic reducing agent such as pyrogallol, hydroquinone, or metol, together with sodium sulfite, which prevents the too rapid oxidation of the reducing agent, and sodium carbonate, which accelerates the rate of reduction. The developer is allowed to act upon the emulsion only long enough to bring out the image; otherwise, if development is prolonged, the unexposed silver halide is likewise reduced to silver, producing the black deposit known as chemical fog. After development the unaffected silver halide is

**Exposure of plate.** When the light-sensitive plate or



FIG. 226. The positive print



removed by immersing in a solution of sodium thiosulfate (hypo), which does not affect the silver image. Alum and other chemicals are sometimes added to the hypo solution in order to harden the gelatin film. The plate is now said to be *fixed*. It is then washed with water and dried.

**Positive and negative processes.** The image so prepared is called a *negative* (Fig. 225), because on looking through it the blackest portions correspond to the brightest parts of the object, and vice versa.

By placing the negative in contact with another light-sensitive surface and exposing it to the light a *positive* print (Fig. 226) is obtained from the negative after the exposed surface is developed. Positives may be made on paper, film (motion-picture film), glass (lantern slides), cloth, or any other rigid material. After exposure the positive image is invisible and is developed in the same way as a negative image. A silver chloride emulsion, however, produces a visible image on exposure to sunlight, and such an emulsion is termed a "printing-out" emulsion as against "developing-out" emulsions. Silver images are often toned by immersing in a solution of a salt of gold or platinum or in one of the solutions of ferrocyanides of certain metals dissolved in suitable solvents, when the silver image is either wholly or partially replaced by the colored metal or colored ferrocyanide.

### EXERCISES

1. Why has copper or bronze been used for so long a time?
2. Why do we have so many relics from the bronze age and so few from the iron age?
3. Why is a solution of copper sulfate acid to litmus paper?
4. How should you account for the fact that so many different salts of copper have the same blue color in dilute solutions?
5. Calomel and corrosive sublimate are both white solids. How could you distinguish between them?
6. Crude silver usually contains iron and lead. What would become of these in refining silver by *parting* with sulfuric acid?
7. Mercuric nitrate and silver nitrate are both white soluble solids. How could you distinguish between them?
8. How do you account for the fact that a silver spoon gradually darkens when in contact with eggs?

9. Why do copper, mercury, and silver all occur to some extent in the free state?

10. What properties make mercury useful in thermometers and in barometers?

11. Write equations for the action of concentrated sulfuric acid on mercury; of nitric acid on silver.

12. Suggest a method for obtaining pure silver from a silver coin.

13. When a solution of silver nitrate is added to a solution of potassium chlorate, no precipitate forms. How do you account for the fact that a precipitate of silver chloride is not formed?

14. Which of the ores of copper contains the largest percentage of copper?

15. What would be the effect of immersing an unexposed photographic film in a solution of sodium thiosulfate?

16. Could a print be toned by using a salt of aluminum or copper?

17. Suppose you dissolved each of the metals copper and mercury in nitric acid, evaporated the solution to dryness, and strongly ignited the residue. What would be left in each case?

18. Suppose you wish to prepare 1000 g. of calomel; what substances and what weight of each would be required?

19. A silver dollar weighs approximately 26.5 g. What weight of silver nitrate could be prepared from such a coin?

20. What weight of cinnabar is needed to produce a *flask* of mercury?

## CHAPTER XLI

### TIN; LEAD

	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	COMMON OXIDES
Tin . . . .	Sn	118.70	7.31	231.85°	SnO            SnO <sub>2</sub>
Lead . . . .	Pb	207.22	11.34	327.5°	PbO   Pb <sub>3</sub> O <sub>4</sub> PbO <sub>2</sub>

**General.** The elements of smaller atomic weight in Group IV of the periodic classification, including carbon, silicon, titanium, and zirconium, are acid-forming in character and have already been described. The elements of greater atomic weight, of which tin and lead are the well-known representatives, are essentially metals. Germanium is intermediate in character and is so rare as to require little comment, while thorium is a metal and is also very rare. These four elements are not so closely related to each other as are the members of some other groups, and each has its own peculiarities. The more abundant elements, tin and lead, will be described first.

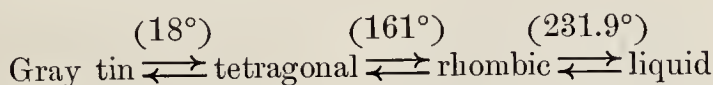
### TIN

**History and occurrence.** It is difficult to decide just when tin became known to the ancients, but it was undoubtedly at a very early date. In ancient times it was frequently confused with lead; the distinction between the two first clearly appeared in the writings of Pliny, about the beginning of the Christian Era. It is found chiefly as the oxide SnO<sub>2</sub>, called *cassiterite* or *tinestone*, and this is the only commercial ore. Malaya stands first in production, followed by Bolivia, Banca, and China.

Its production in the United States is insignificant. Normally the world's annual production of tin is about 250,000,000 lb.

**Metallurgy.** Since tin occurs as the oxide and is relatively free from other metals, its metallurgy is very simple and consists in reducing the ore with carbon. In some cases the ore is first roasted, to free it from sulfur and arsenic.

**Properties.** Tin occurs in a number of allotropic forms, which pass into each other at definite transition temperatures, the order being as follows:



The first of these transitions is the most interesting, since it takes place at ordinary temperatures. Below 18° ordinary white, or tetragonal, tin is an unstable form and under some conditions changes into the gray modification, at the same time losing its metallic appearance and crumbling into a powder. The usual form is silver white, is harder than lead, and is quite malleable. The bending of a bar of tin is accompanied by a creaking noise called *tin cry*. The metal melts at 231.85° and boils at about 2260°. Its average density is 7.31.

**Tin plague.** The transformation of white tin into the gray form is sometimes a serious matter. It was first noticed in connection with the deterioration of some organ pipes made of tin, which developed holes and then broke up completely. Later, ingots of tin stored in a Russian customhouse during a very cold winter were found to have crumbled to powder. When the transformation once starts, it continues to spread as long as the temperature is below 18°, and this uncontrollable spread has been called the tin plague, or museum disease, since it sometimes spreads over tin objects in a museum (Fig. 227). The speed of the transformation is increased by contact with a solution of certain salts in which tin is slightly soluble.

**Chemical conduct.** At ordinary temperatures tin undergoes almost no change in the air, nor is it attacked by the combined action of air and water; at higher temperatures it is covered



with a film of oxide. Dilute acids act upon it very slowly, evolving hydrogen; concentrated hydrochloric acid acts more rapidly, forming the chloride  $\text{SnCl}_2$ . Oxidizing acids, such as nitric acid, convert it into a hydrate of the oxide  $\text{SnO}_2$ .

**Uses of tin.** The great use for tin is in the making of *tin plate*. The process consists in dipping thin sheets of iron into the melted tin and is quite similar to that of galvanizing

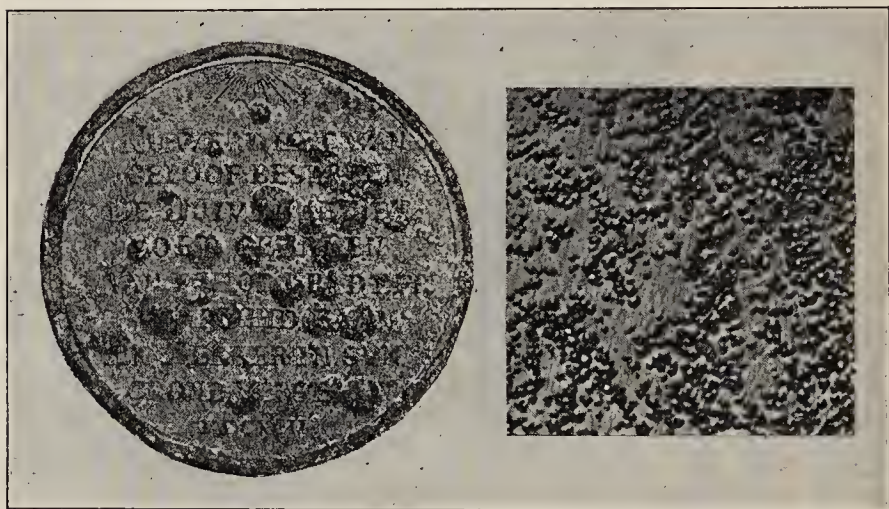


FIG. 227. Tin objects in a museum, showing the transformation of white tin into the gray form (museum tin disease)

iron (p. 485). Owing to its resistance to the action of air and weak acids, tin plate is used in many ways, such as in roofing and in the manufacture of tin cans, cooking vessels, and similar articles. Small pipes of block tin are used instead of lead for conveying pure water or liquids containing dilute acids, such as soda water. Hammered until very thin, it forms *tin foil*, used as wrappers for various articles. Some tin foil contains the cheaper metal lead. Many useful alloys contain tin (p. 552). *Pewter* and *soft solder* are alloys of tin and lead.

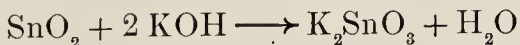
**Rusting of tin plate.** If the coating of tin on tin plate is scratched through to the iron, the iron will rust faster than if there were no tin covering. The two metals and the water constitute a battery,

much like the Daniell cell (p. 555), and in a battery the metal highest in the electrochemical series is the one that is corroded. In the case of galvanized iron the zinc rusts first, and the iron resists rusting as long as any zinc is present.

**Soldering and brazing.** The use of solder in joining two metal surfaces depends upon (1) the low melting point of the solder and (2) the fact that it flows over *clean* metal surfaces and sticks to them on cooling. To secure clean surfaces free from oxide, a suitable flux must be used which will either *dissolve* the oxide as fast as it forms or will *reduce* it again to metal. The usual fluxes are zinc chloride, ammonium chloride, rosin, and stearin. In *brazing*, or *hard soldering*, the process is essentially the same, except that a low-melting brass is used instead of solder, and borax is used as a flux.

**Compounds of tin.** Tin forms two series of compounds: the *stannous*, in which the tin is bivalent, illustrated in the compounds  $\text{SnO}$ ,  $\text{SnS}$ ,  $\text{SnCl}_2$ ; the *stannic*, in which it is quadrivalent, as shown in the compounds  $\text{SnO}_2$ ,  $\text{SnS}_2$ . There is also an acid,  $\text{H}_2\text{SnO}_3$ , called *stannic acid*, which forms a series of salts called *stannates*. Only a few compounds of tin need be described.

**Stannic oxide ( $\text{SnO}_2$ ).** Stannic oxide is of interest, since it is the chief compound of tin found in nature. It is sometimes found in good-sized crystals, but as prepared in the laboratory it is a white powder. When stannic oxide is fused with potassium hydroxide it forms *potassium stannate*, acting very much like silicon dioxide:



**Stannic acid ( $\text{H}_2\text{SnO}_3$ ).** The compound  $\text{H}_2\text{SnO}_3$  can be prepared in a number of ways; it is a white solid, insoluble in water. It is a remarkable fact that its chemical properties depend to a great extent upon the way in which it is made. Some methods yield a product that is readily soluble in dilute acids, while the product formed by the action of concentrated nitric acid upon tin is insoluble in acids and is called *meta-stannic acid*. The soluble forms are colloidal in character, and

it is probable that the differences in the precipitated colloids are due to the size of the particles formed rather than to a different chemical structure of the compounds.

**Chlorides of tin.** Stannous chloride is prepared by dissolving tin in concentrated hydrochloric acid and evaporating the solution to crystallization. The crystals which are obtained have the composition  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and are known as *tin crystals*. By treating a solution of stannous chloride with aqua regia, stannic chloride is formed:

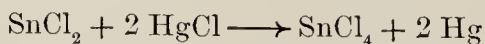


The salt which crystallizes from such a solution has the composition  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  and is known commercially as *oxymuriate of tin*. If metallic tin is heated in a current of dry chlorine, the anhydrous chloride ( $\text{SnCl}_4$ ) is obtained as a heavy, colorless liquid which fumes strongly on exposure to air. A great deal of stannic chloride is recovered from scrap tin plate by *detinning* with chlorine.

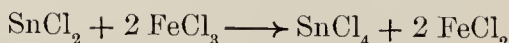
**Reducing properties of stannous chloride.** The ease with which stannous chloride takes up chlorine to form stannic chloride makes it a good reducing agent in many reactions, changing the higher chlorides of metals to lower ones. Thus, mercuric chloride is changed into mercurous chloride:



If the stannous chloride is in excess, the reaction may go farther, producing metallic mercury:



Ferric chloride is in like manner reduced to ferrous chloride:



**Uses of compounds of tin.** The chlorides of tin, as well as the alkali stannates, are much used as mordants in dyeing processes. The hydroxides of tin and free stannic acid, which are easily liberated from these compounds, possess in very marked degree the power of fixing dyes upon fibers, as explained under aluminum

(p. 498). Stannic chloride is used for *weighting* silk, or giving it more body. In the World War stannic chloride was filled into hand grenades and used to clear dugouts of enemy troops. The explosion of the grenades filled the dugouts with a fine mist of the chloride, and in this way vitiated the air so that one could not breathe it without painful suffocation.

**Other compounds of tin.** A few of the other important compounds are included in the following list:

Stannous sulfide ( $\text{SnS}$ ): a nearly black precipitate formed by the action of hydrogen sulfide upon a stannous salt

Stannic sulfide ( $\text{SnS}_2$ ): a bright-yellow precipitate formed by the action of hydrogen sulfide upon a stannic salt; also obtained in the form of golden-bronze scales known as *mosaic gold*

Ammonium chlorostannate ( $(\text{NH}_4)_2\text{SnCl}_6$ ): a well-crystallized salt used as a mordant in dyeing and called *pink salt*

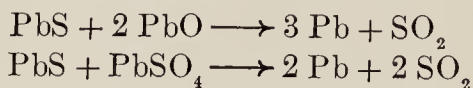
## LEAD

**History and occurrence.** Articles made of lead have been found in Egyptian ruins of great antiquity, and there is no doubt that metallic lead found applications from very early times. The Romans called it *plumbum* and used it for water conduits as we do today. It does not occur to any appreciable extent in the native state, but is found in combination in many parts of the world. The minerals of most importance to metallurgists are *galena*, or *galenite* ( $\text{PbS}$ ), and to a less extent *cerussite* ( $\text{PbCO}_3$ ) and *anglesite* ( $\text{PbSO}_4$ ). The United States produces over one third of the world's output of lead, the chief producing states being Missouri, Idaho, Utah, and Oklahoma. The countries which come next to the United States in production are Spain, Mexico, and Germany.

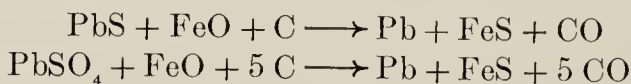
**Metallurgy.** Galenite often contains some silver and gold, and silver ores are often purposely combined with lead ores and the two smelted together. When no silver is present, the ores are roasted in an open oven until they are partially oxidized, and the lead is present as a mixture of sulfide, sulfate, and



oxide. Access of air is then cut off and the temperature raised, when the reactions represented in the following equations take place :



Silver-bearing ores are worked in a blast furnace, the bottom of which consists of a large crucible constructed of fire brick. The ore is first roasted and is then charged into the furnace, together with coke and a flux consisting of limestone and iron ore. The chief reactions which produce lead are represented in the following equations :



The liquid lead, in which are dissolved the gold and silver, together with varying quantities of copper, antimony, arsenic, and bismuth, collects in the crucible and is tapped off.

**Refining of lead.** The lead obtained in this way is called *hard* lead because of the effect of the alloyed metals. It is softened by the removal of these as follows: The hard lead is melted in a reverberatory furnace with free access of air until the copper, arsenic, and antimony are oxidized, together with a considerable quantity of lead. The oxides are skimmed off and the softened lead, which contains the silver, gold, and also bismuth, is run off for desilverizing. Two processes for this purpose are in use in this country.

1. **The Parkes process.** In the Parkes process the lead is run into kettles holding as much as 30 tons, and about 1 per cent of its weight of zinc is added and thoroughly stirred in. These two metals do not mix to any great extent, and gold and silver, as well as copper, are much more soluble in zinc than in lead. Consequently, when the stirring ceases, the zinc, together with most of the precious metals, rises to the top and, when the melt is allowed to cool, hardens to a crust which can be skimmed off. The process is repeated several times. The zinc remaining in the lead is removed by blowing dry steam and air through the liquid

lead, which oxidizes the zinc; or it is oxidized as in the original softening. The zinc crusts are distilled from a retort; by this process the zinc is recovered, to be used again, and the residue is cupeled, as with silver, to give *doré* bars.

**2. The Betts process.** In the Betts process the lead is refined by electrolysis, as in the case of copper. A sheet of pure lead serves as cathode, a thick plate of crude lead as anode, and a solution of lead fluosilicate ( $\text{PbSiF}_6$ ), together with some colloidal material, such as gelatin, as electrolyte. The lead deposits upon the cathode, the iron remains dissolved in the electrolyte, and the copper, bismuth, antimony, arsenic, silver, and gold are left undissolved as a skeleton of the anode. A considerable quantity of bismuth is recovered from this source.

**Properties of lead.** Pure lead is a silvery metal of density 11.34, which melts at  $327.5^\circ$  and boils at  $1620^\circ$ . It is dimorphous, crystallizing either in the isometric or in the monoclinic system. It is the softest of all the heavy metals and is a moderately good conductor of electricity. It is quite malleable but has little strength.

**Chemical conduct.** Lead is a moderately active metal, standing next above hydrogen in the electrochemical series. Its true activity is often concealed by the fact that so many of its compounds are insoluble and form protective coatings upon its surface. It quickly tarnishes in air, owing to the formation of a bluish-gray oxide ( $\text{Pb}_2\text{O}$ ). With the exception of hydrochloric and sulfuric acids, which form insoluble compounds with lead, most acids (even very weak ones) act upon it, forming soluble lead salts. Hot concentrated hydrochloric and sulfuric acids also attack it slightly.

**Uses of lead.** The industrial uses of lead are very numerous. The paint industry is the largest consumer, closely followed by the storage battery. It is also used in the manufacture of water pipes and of structures to be exposed to acids, such as the lead chambers in a sulfuric-acid plant. A great many alloys contain lead, among them being type metal, antifric-tion metals of various kinds, shot, pewter, and solder (p. 337).

**Compounds of lead.** In nearly all its compounds lead is bivalent, but in a few it has a valence of four. All its compounds are poisonous.

**Lead oxides.** Lead forms a number of oxides, the most important of which are the following:

1. *Litharge, massicot* ( $PbO$ ). This oxide forms when hot lead is oxidized in the air at a temperature a little less than  $1000^{\circ}$ . If the temperature is high enough to melt the oxide, the color of the product is deep yellow or even red, and the oxide is called *litharge*. It is used in the preparation of boiled linseed oil and in glassmaking. If the oxide is not melted, it forms a light yellow powder called *massicot*, which is used in making red lead.

2. *Red lead, or minium* ( $Pb_3O_4$ ). Minium is prepared by heating lead (or massicot) to about  $450^{\circ}$  in contact with a current of air. It is a heavy powder of a beautiful red color and is much used as a pigment for painting structural iron. Mixed with linseed oil it forms a cement used in joining gas pipes.

3. *Lead peroxide* ( $PbO_2$ ). This is left as a residue when minium is heated with nitric acid:



It is a brown powder which easily gives up a part of its oxygen and, like manganese dioxide and barium dioxide, is a good oxidizing agent.

**Lead sulfide** ( $PbS$ ). In nature this compound occurs in a highly crystalline form called *galenite*, the crystals having much the same color and luster as pure lead. It is readily prepared in the laboratory as a black precipitate, by the action of hydrogen sulfide upon soluble lead salts:



It is insoluble both in water and in cold dilute acids.

**Lead carbonate.** While the normal carbonate of lead,  $PbCO_3$ , is found to some extent in nature and can be prepared in the laboratory, basic carbonates of varying composition

are much more easy to obtain. One of the simplest of these has the composition  $2 \text{PbCO}_3 \cdot \text{Pb(OH)}_2$  and is called *white lead*. This has long been prepared on a large scale as a white pigment and as a base for paints which are to be colored with other substances.

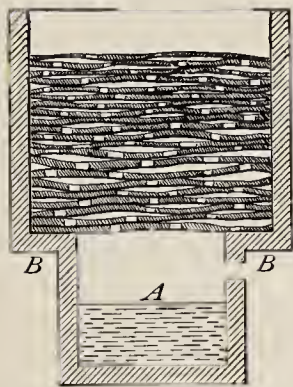


FIG. 228. A crock filled with thin lead plates (buckles) for making white lead

supporting the plates. Under them in *A* is poured a suitable quantity of dilute acetic acid, and the crocks so charged are placed in banks and covered with stable manure or spent tanbark. The heat of fermentation in the latter warms the acid, the fumes of which attack the lead, forming lead acetate. The carbon dioxide from the fermentation enters into reaction with the acetate, producing the basic carbonate and regenerating acetic acid. This acid acts again upon the lead, and the process continues until the buckles are

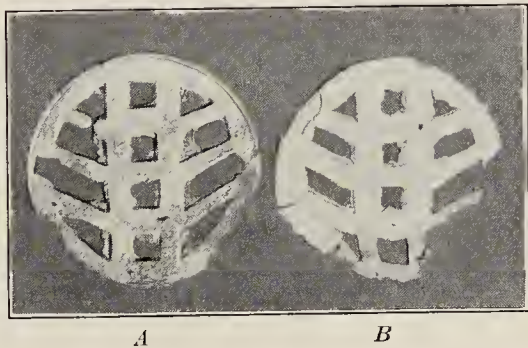


FIG. 229. Lead buckles before (*A*) and after (*B*) exposure to acetic acid and carbon dioxide

almost completely converted into the desired compound. Fig. 229, *A* shows a lead buckle before exposure to acetic acid and carbon dioxide; *B* shows the appearance of the same buckle after such exposure, the white carbonate somewhat resembling enamel.



Electrolytic processes for making white lead are used to a limited extent, but the great percentage of the white lead used in paints is still prepared by the old Dutch process.

**Other important compounds of lead.** Soluble salts of lead are obtained by dissolving litharge in the appropriate acid. Insoluble salts are obtained by precipitation. Some of the most important are the following:

Lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ): white soluble crystals

Lead chloride ( $\text{PbCl}_2$ ): white needles, very sparingly soluble in cold water and readily so in hot water

Lead sulfate ( $\text{PbSO}_4$ ): an insoluble white crystalline powder

Lead acetate ( $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{H}_2\text{O}$ ): a soluble white salt called *sugar of lead* (p. 413)

Lead chromate ( $\text{PbCrO}_4$ ): a yellow solid used as a pigment in paint (*chrome yellow*)

## PAINTS

**Composition.** A paint consists of two essential ingredients: the *vehicle* and the *pigment*.

1. **The vehicle, or liquid medium.** This must be an oil *which will dry rapidly and harden in drying to a more or less flexible, hornlike body*. These changes in the oil are due to oxidation by the air. A number of different oils will serve this purpose, but linseed oil and Chinese wood oil (tung oil) are at present the standard drying oils, since they can be produced in quantity and at moderate cost. It is customary to add to it a *dryer*, made by boiling some of the oil with oxides of manganese, lead, or cobalt. The oxides enter into combination with the oil and assist catalytically in its oxidation.

2. **The pigment.** The body of the paint must be some solid material, suspended in the oil, which will give a smooth and waxy surface as the paint dries. It must also have good covering power; that is, it must cover over the surface of any object being painted. Barium sulfate, for example, is a white solid not acted upon by air and fumes (very desirable properties in a pigment); yet it cannot be used alone as a pigment, since it does not have this covering power. The pigment may be (1) a white solid, such as white lead, zinc oxide, a mixture of zinc sulfide and barium sulfate (*lithopone*, p. 486), or a mixture of titanium oxide (p. 347) and

barium sulfate (*titanox*); or it may be (2) a colored compound such as certain iron oxides; or it may be (3) a mixture of both the white and the colored materials. Most colored paints consist of a white base, which is given the desired color by the addition of an appropriate colored pigment. Sometimes these pigments are prepared by precipitating an amorphous body (usually a colloid) in the presence of an organic dye, the dye being adsorbed by the precipitate, coloring it. Such pigments can be prepared in endless variety of colors and are called *lakes*. They are usually not so permanent as mineral pigments but serve the purpose very well.

**Varnish.** Varnish is a liquid which, on being applied to a surface and allowed to stand, forms a closely adhering and generally transparent film. Varnishes are made by dissolving in appropriate solvents the resins (or gums) obtained from certain trees. The best varnish is made by dissolving a resin in linseed oil or Chinese wood oil (*tung*

oil) and *thinned* with turpentine or benzine. On exposure to air the turpentine evaporates and the oil oxidizes and dries as in paints.

**Lacquers.** The modern lacquers used so extensively, especially in the automobile industry, have as their base nitrocellulose dissolved in a low-boiling ester or mixture of esters (p. 415). In addition they also contain (1) camphor or some similar substance to prevent cracking; (2) resin, to give luster and hardness; and (3) a weak base to prevent decomposition of the nitrocellulose. If a colored lacquer is desired, a pigment of the appropriate color must be added. Many pigments are used, both organic and inorganic.

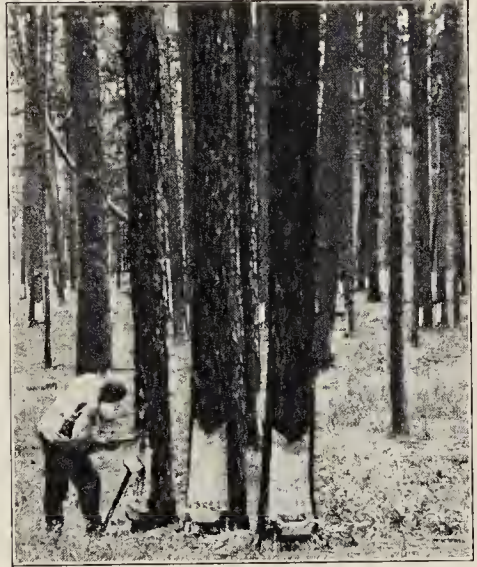


FIG. 230. View in a Southern pine forest utilized for the production of rosin and turpentine

Incisions are made in the trees, and from these incisions exudes a resinous mass which is the raw material from which the rosin and oil of turpentine are obtained by distillation

**Storage cell.** The storage cell, or accumulator, plays an important part in modern electrical developments. Its fundamental characteristic is that the chemical action upon which it depends is reversible. The chemical action taking place when

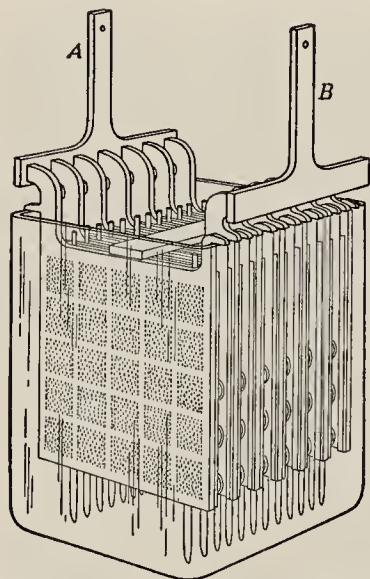


FIG. 231. A seven-plate storage battery

the cell is delivering current is reversed when a current is conducted through the cell in an opposite direction. Electrical energy can therefore be stored in the cell as chemical energy and drawn off again, when desired, as electrical energy.

In the ordinary accumulator (Fig. 231) the electrodes are made of a skeleton of lead. When ready for use, the one plate is covered with a thick deposit of spongy lead, which is the active material; the other is similarly covered with a layer of lead dioxide. The electrolyte is moderately dilute sulfuric acid ( $\text{H}^+\text{H}^+$ ,  $\text{SO}_4^{--}$ ). A number

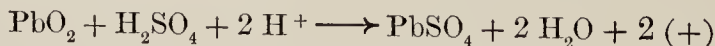
of pairs of such plates are arranged together in one cell. When these pairs are connected by a wire, the reactions are as follows:

At the lead plate:

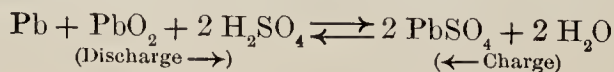


The insoluble lead sulfate deposits in the spongy lead, and the negative charge (2 electrons) is given up to the plate.

At the lead dioxide plate:

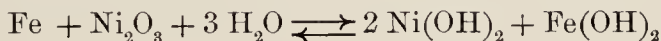


The lead sulfate deposits with the dioxide, and the positive charge is given up to the plate (2 electrons withdrawn from it). The electrons flow through the external circuit from the lead plate to the dioxide plate. The complete equation is therefore



It will be seen that the action of the cell results in bringing the two plates to an identical condition and in withdrawing sulfuric acid from the electrolyte. The cell is never allowed to come entirely to this discharged condition. When the current is reversed, the two plates are restored to their original state.

In the Edison cell the one plate is of iron, the other is covered with a deposit of the higher oxide of nickel ( $\text{Ni}_2\text{O}_3$ ), and the electrolyte is a solution of potassium hydroxide. The reactions are not so well understood as in the case of the lead battery, but in a general way the following equation represents the reversible reaction:



### GERMANIUM AND THORIUM

**Germanium.** Although germanium was discovered by the German chemist Winkler in 1886, it has been so rare that little has been added to our knowledge of the metal until recent years. It has now been found to be present in appreciable quantities in the residues obtained in the distillation of zinc, and the American chemist Dennis has succeeded in preparing it from this source by an improved method. It resembles tin more closely than any other metal, both in its properties and in its chemical conduct.

**Thorium.** Discovered nearly a century ago (in 1828) by the Swedish chemist Berzelius, thorium remained a chemical curiosity until the development of the gas-mantle industry brought it into prominence. It is a constituent of a number of rare minerals, but commercially it is nearly all obtained from monazite sand (p. 386). The metal is extremely difficult to prepare in pure form. Its melting point is not far from that of platinum, and the metal resembles platinum in its physical properties. It is quadrivalent in all its compounds, and it plays the part of a base in all of them. Its oxide,  $\text{ThO}_2$ , is the chief component of the ordinary gas mantle.

Thorium is remarkable for possessing the property of *radioactivity*. This property is more conveniently described in connection with uranium and radium, and the radioactivity of thorium will be referred to in a later chapter.



## EXERCISES

1. Silicon belongs in the same family with tin and lead (p. 259). Point out any resemblance in the chemical conduct of these three elements.

2. (a) Give the names and formulas of the insoluble sulfates. (b) Could lead nitrate be used in place of barium chloride in testing for sulfates?

3. Contrast the action of hydrochloric acid on tin, mercury, zinc, and aluminum.

4. Name the important alloys of tin.

5. Contrast the action of hydrochloric acid upon  $\text{PbO}_2$ ,  $\text{MnO}_2$ , and  $\text{BaO}_2$ .

6. How could you distinguish between red lead, Venetian red, and vermilion?

7. How could you distinguish between tin and aluminum? between lead and silver?

8. Which pigment should you prefer for painting the interior of a chemical laboratory, white lead, zinc oxide, or lithopone?

9. White lead is sometimes adulterated with barytes. Suggest a method for detecting the barytes, if present in any given sample.

10. What weight of cassiterite would be required to make 100 kg. of Babbitt metal?

11. What weight of lead is necessary for the manufacture of 1000 kg. of white lead?

12. Sugar of lead is prepared by treating litharge with acetic acid. What weight of litharge is necessary for the preparation of 1000 kg. of lead acetate, assuming that all the lead in the litharge is converted into lead acetate?

13. The purity of white lead is usually determined by observing the volume of carbon dioxide, given off when it is treated with an acid. On the supposition that it has the formula  $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ , how nearly pure was a sample if 1 g. gave 30 cc. of carbon dioxide at  $20^\circ$  and 750 mm.?

## CHAPTER XLII

### MANGANESE ; CHROMIUM

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT	FORMULAS OF ACIDS
Manganese	Mn	54.93	7.2	1260°	H <sub>2</sub> MnO <sub>4</sub> and HMnO <sub>4</sub>
Chromium	Cr	52.01	7.1	1615°	H <sub>2</sub> CrO <sub>4</sub> and H <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>

**General.** Manganese and chromium, while belonging to different families, have so many features in common in their chemical conduct that they may be studied together with advantage. They differ from most of the elements so far studied in that they have high valences in which they act as *acid-forming* elements, and low valences in which they act as *base-forming* elements. The change from one of these valences to the other is readily brought about, so the compounds of these two elements tend to take part in many reactions of *oxidation and reduction*. It is such reactions that constitute the commercial value of many of their salts.

Elements like manganese and chromium, which in elementary form have the properties of metals, but which are capable of forming acids in higher states of valence, are called *metallo-acid* elements.

#### MANGANESE

**Occurrence.** Manganese is found in nature chiefly as the dioxide MnO<sub>2</sub>, called *pyrolusite*. In smaller quantities it occurs as the oxides Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub> and as the carbonate MnCO<sub>3</sub>. Some iron ores contain manganese. In the United States, Montana and Minnesota lead in the production of manganese, but the largest part of our supply comes from India and Brazil.

**Properties and preparation.** In a general way manganese resembles iron, being of about the same density and color; but it is harder, more fusible, more crystalline, and more readily acted upon by air and moisture. Acids readily dissolve it, forming manganous salts. The element is difficult to prepare in pure condition and has no commercial applications. It can be prepared, however, by reducing the oxide with aluminum powder (p. 496) or by the use of the electric furnace, with carbon as the reducing agent. By reducing a mixture of the oxides of iron and manganese an alloy known as *ferromanganese* is obtained. About 95 per cent of the world's production of manganese is used in this form as a purifier in making steel. About 14 lb. of manganese is used for every ton of steel produced.

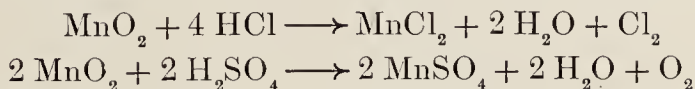
**Oxides of manganese.** The following oxides of manganese are well known:  $\text{MnO}$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{MnO}_2$ , and  $\text{Mn}_2\text{O}_7$ . Only one of these, the dioxide, needs special mention.

**Manganese dioxide (pyrolusite) ( $\text{MnO}_2$ ).** This substance is the most abundant manganese compound found in nature and is the ore from which all other compounds of manganese are made. It is a hard, brittle, black substance which is valuable as an oxidizing agent. It will be recalled that it is used in the laboratory preparation of chlorine and oxygen, in decolorizing glass which contains iron, and in the manufacture of ferromanganese. It is also extensively used in the manufacture of dry-cell electric batteries.

**Compounds containing manganese as a base-forming element.** As a base-forming element manganese forms two series of salts, in one of which it is bivalent and in the other trivalent. The most important of these salts, all of which belong to the *manganous* series, are the following:

Manganous chloride . . . . .	$\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$
Manganous sulfide . . . . .	$\text{MnS}$
Manganous sulfate . . . . .	$\text{MnSO}_4 \cdot 4 \text{H}_2\text{O}$
Manganous carbonate . . . . .	$\text{MnCO}_3$
Manganous hydroxide . . . . .	$\text{Mn(OH)}_2$

The well-crystallized manganous salts are rose-colored. The manganous salts not only have formulas similar to the ferrous salts but resemble them in many of their chemical properties. The chloride and the sulfate may be prepared by heating the dioxide with hydrochloric and sulfuric acid respectively :

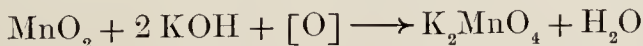


The sulfide, carbonate, and hydroxide, being insoluble, may be prepared from a solution of the chloride or the sulfate by precipitation with the appropriate reagents.

**Compounds containing manganese as an acid-forming element.**

Manganese forms two unstable acids: namely, *manganic acid* ( $\text{H}_2\text{MnO}_4$ ) and *permanganic acid* ( $\text{HMnO}_4$ ). While these acids are of little interest, some of their salts, especially the permanganates, are important compounds.

**Manganic acid and manganates.** When any compound of manganese, such as manganese dioxide, is fused with an *alkali and an oxidizing agent*, a green compound is formed. The equation, when caustic potash is used, is as follows:



The green compound,  $\text{K}_2\text{MnO}_4$ , is called *potassium manganate* and is a salt of the unstable *manganic acid*. The manganates, as well as the free acid, are all very unstable, and as a consequence are good oxidizing agents.

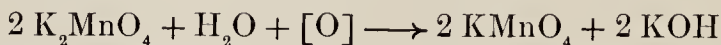
**Permanganic acid and the permanganates.** When potassium manganate is treated with water a reversible decomposition takes place which can be expressed by the equation



If an acid is now added, the potassium hydroxide is neutralized and the reaction goes on to completion, the chief product being *potassium permanganate* ( $\text{KMnO}_4$ ). Since one third of the manganese is lost in this reaction, potassium permanganate is now made by electrolysis. The manganate is dissolved in



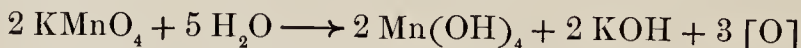
water, and at the anode the oxygen evolved by the electrolysis of water acts upon the manganate in the following way:



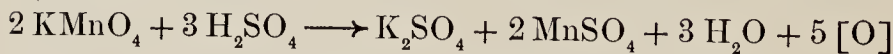
Potassium permanganate crystallizes in dark-purple needles and is very soluble in water, forming an intensely purple solution. All other permanganates, as well as permanganic acid itself, are very soluble and give solutions of the same color.

**Oxidizing properties of the permanganates.** The permanganates are remarkable for their strong oxidizing properties. When used as an oxidizing agent the permanganate is itself reduced, the exact character of the products formed from it depending upon whether the oxidation takes place (1) in an alkaline or neutral solution or (2) in an acid solution.

1. *Oxidation in alkaline or neutral solution.* When the solution is either alkaline or neutral, *the potassium and the manganese of the permanganate are both converted into hydroxides*, as shown in the equation

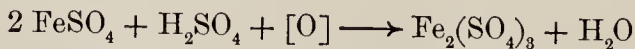


2. *Oxidation in acid solution.* When free acid such as sulfuric acid is present, *the potassium and the manganese are both changed into salts of the acid*:

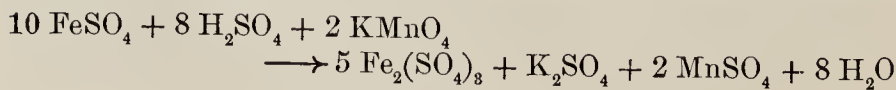


*Under ordinary conditions neither reaction takes place except in the presence of a third substance which is capable of oxidation. The oxygen is not given off in the free state, as the equations show, but is used up in effecting oxidation.*

For example, if ferrous sulfate is oxidized to ferric sulfate, we have the equation (p. 540)



Combining this equation with the last equation given above, we have



Potassium permanganate ( $\text{KMnO}_4$ ) is particularly valuable as an oxidizing agent, not only because it acts readily either in acid or in alkaline solution but also because the reaction takes place so easily that often it is not even necessary to heat the solution to secure action. The substance finds many uses in the laboratory, especially in analytical work. It is also used as an antiseptic and as a disinfectant. Sodium permanganate ( $\text{NaMnO}_4$ ) is very difficult to crystallize, so that the solid form is more expensive than the corresponding potassium salt.

### CHROMIUM

**Occurrence.** The ore from which all chromium compounds are made is *chromite*, or chrome iron ore ( $\text{Fe}(\text{CrO}_2)_2$ ). This is found most abundantly in New Caledonia and Rhodesia. The United States has produced little except during the period of the World War, when the prices were inflated and foreign supplies hard to obtain. The element also occurs in small quantities in many other minerals, especially in *crocoite* ( $\text{PbCrO}_4$ ), in which it was first discovered.

**Properties and preparation.** Chromium is a very hard metal of about the same density and melting point as iron. At ordinary temperatures air has little action upon it; at higher temperatures, however, it burns brilliantly. Nitric acid has no action upon it, but hydrochloric and dilute sulfuric acids dissolve it, liberating hydrogen and forming chromous salts. Chromium, like manganese, is very hard to reduce from its ores, owing to its great affinity for oxygen. It can, however, be made by the same methods which have proved successful with manganese.

Chromium is a valuable metal for producing certain steel alloys. It also forms desirable alloys with other metals such as copper and nickel. In recent years it has come into extensive use in electroplating. While it is more expensive for this purpose than nickel, nevertheless chromium plating is much more resistant to change than is nickel.

**Compounds containing chromium as a base-forming element.**

While chromium forms two series of salts, in which it acts as a bivalent and as a trivalent element, chromous salts are difficult to prepare in the solid state and are of little importance. The most important of the chromic series are the following:

Chromic hydroxide . . . . .	$\text{Cr}(\text{OH})_3$
Chromic sulfate . . . . .	$\text{Cr}_2(\text{SO}_4)_3$
Chromic chloride . . . . .	$\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$
Potassium chrome alum . . . . .	$\text{KCr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$

**Chromic oxide ( $\text{Cr}_2\text{O}_3$ ).** Chromic oxide is a green powder which can be prepared by the various methods available in the preparation of oxides. Its exact shade depends upon its method of preparation; this fact is important in its use as a pigment.

**Chromium hydroxide.** When we attempt to prepare the insoluble hydroxide  $\text{Cr}(\text{OH})_3$  we get a green gel which has a variable formula and is best considered as a hydrated oxide (p. 538). This compound appears to dissolve in alkali, but it is probable that it is merely peptized to a colloidal dispersion. If we fuse the oxide with a base, we obtain definite salts which are derived from the oxide-hydroxide  $\text{CrO} \cdot \text{OH}$ , called chromous acid. The ferrous salt of this acid,  $\text{Fe}(\text{CrO}_2)_2$ , is the mineral *chromite*.

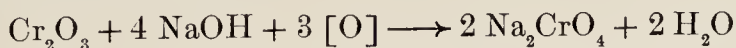
**Chromic sulfate ( $\text{Cr}_2(\text{SO}_4)_3$ ).** This compound is a violet-colored solid which dissolves in water, forming a solution of the same color. This solution, however, turns green when heated, owing to the formation of basic salts.

Chromic sulfate, like ferric and aluminum sulfates, unites with the sulfates of the alkali metals to form alums, of which *potassium chrome alum* ( $\text{KCr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ ) and *ammonium chrome alum* ( $\text{NH}_4\text{Cr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ ) are the best known. These form beautiful dark-purple crystals and have some practical uses in the tanning industry and in photography. A number of the salts of chromium are also used in the dyeing industry, for they hydrolyze like aluminum salts, and the hydrated oxide forms a good mordant.

**Hydrolysis of chromium salts.** When ammonium sulfide is added to a solution of a chromium salt, such as the sulfate, the hydrated oxide is precipitated instead of the sulfide. This is due to the fact that chromic sulfide, like aluminum sulfide, hydrolyzes in the presence of water. Similarly, a soluble carbonate precipitates a basic carbonate of chromium.

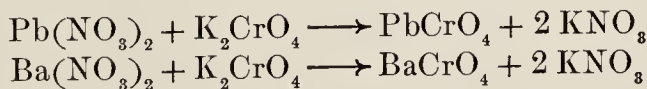
**Compounds containing chromium as an acid-forming element.** Like manganese, chromium forms two unstable acids; namely, *chromic acid* and *dichromic acid*. Their salts, the *chromates* and *dichromates*, are important compounds.

**Chromates.** When a chromium compound is fused with an alkali and an oxidizing agent, a chromate is produced. When sodium hydroxide is used as the alkali, together with chromic oxide, the equation is



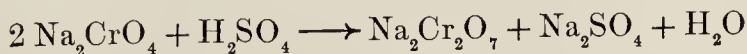
This reaction recalls the formation of a manganate.

**Properties of chromates.** The chromates are salts of the unstable *chromic acid* ( $\text{H}_2\text{CrO}_4$ ) and as a rule are yellow in color. Potassium chromate ( $\text{K}_2\text{CrO}_4$ ) and sodium chromate ( $\text{Na}_2\text{CrO}_4$ ) are freely soluble in water, but most of the chromates are insoluble and can be prepared by precipitation. Thus, when a solution of potassium chromate is added to a solution of lead nitrate or of barium nitrate, the reactions expressed by the following equations occur:



Lead chromate (*chrome yellow*) and barium chromate separate as yellow precipitates. The presence of either of these two metals can be detected by taking advantage of these reactions.

**Dichromates.** When sodium chromate or potassium chromate is treated with an acid, a salt of the unstable *dichromic acid* ( $\text{H}_2\text{Cr}_2\text{O}_7$ ) is formed:

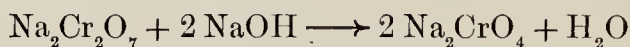




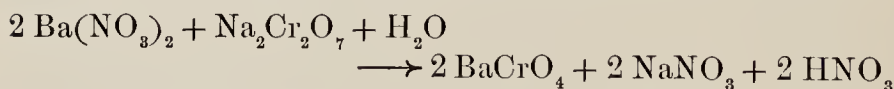
The relation between the chromates and dichromates is the same as that between the phosphates and the pyrophosphates. Sodium dichromate might therefore be called sodium pyrochromate.

Potassium dichromate ( $K_2Cr_2O_7$ ) is the most familiar chromium compound. It forms large crystals of a brilliant red color and is rather sparingly soluble in water. Sodium chromate is much more soluble in water than the potassium salt, and the crystals deposited from the saturated solution are not so well formed and are somewhat deliquescent. They have the formula  $Na_2Cr_2O_7 \cdot 2H_2O$ . The sodium salt is now more widely used than the potassium salt.

**Properties and uses of dichromates.** When a soluble dichromate is treated with a solution of a base, the dichromate is converted into the chromate:

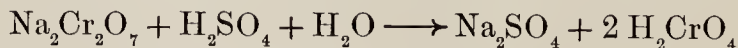


When a solution of a dichromate is added to a solution of a lead or a barium salt, the corresponding chromate (not dichromate) is precipitated. With barium nitrate the equation is



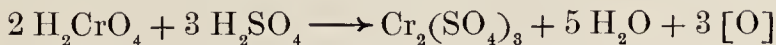
Sodium dichromate finds use in many industries as an oxidizing agent, especially in the preparation of organic substances, such as the dye alizarin. It is also used in preparing pigments and in the process of tanning.

**Oxidizing action of chromates and dichromates.** When a solution of a chromate or of a dichromate is treated with an excess of an acid, chromic acid is set free. With sodium dichromate and sulfuric acid the equation is as follows:

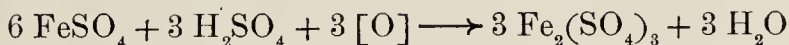


If now there is some material present that is easily oxidized, the chromic acid acts as an oxidizing agent, the chromium

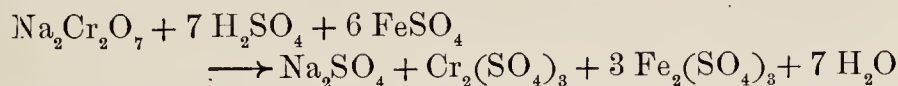
being converted into a tervalent metal in the process. In the presence of sulfuric acid the equation may be written thus



The oxygen is not given off as such, but is taken up by the substance undergoing oxidation. For example, with ferrous sulfate the equation is as follows:



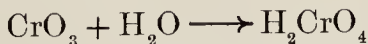
The three equations showing the steps in the oxidizing action of sodium dichromate upon ferrous sulfate may be combined into one equation:



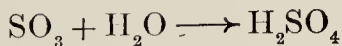
It will be seen that a dichromate decomposes in very much the same way as a permanganate does, *the sodium and chromium being both changed into salts.*

**Potassium chrome alum.** When potassium dichromate and sulfuric acid are used for oxidation, it will be noticed that potassium sulfate and chromium sulfate are formed as the products of the reaction. On evaporating the solution these substances crystallize out as *potassium chrome alum*, which is produced as a by-product in the industries using potassium dichromate for oxidizing purposes. Sodium chromate does not form a similar alum.

**Chromic anhydride ( $\text{CrO}_3$ ).** When *concentrated* sulfuric acid is added to a concentrated solution of potassium dichromate, and the liquid is allowed to stand, deep-red, needle-shaped crystals appear which have the formula  $\text{CrO}_3$ . This oxide of chromium is called *chromic anhydride*, since it combines readily with water to form chromic acid:



It is therefore analogous to sulfur trioxide, which forms sulfuric acid in a similar way:



Chromic anhydride is a very strong oxidizing agent, giving up oxygen and forming chromic oxide:



### MEMBERS OF THE CHROMIUM FAMILY

The elements that fall in the same periodic family with chromium, namely, molybdenum, tungsten, and uranium, are typical *metallo-acid elements*; that is, they form acids as well as salts. In the free state they are high-melting, heavy metals. They form a great variety of compounds, in most of which the elements have a valence of six and play the part of acid-forming elements.

**Molybdenum.** Molybdenum is found chiefly as *molybdenite* ( $\text{MoS}_2$ ). When this mineral is roasted in the air, the oxide  $\text{MoO}_3$  is obtained, and from this oxide other compounds can be prepared. The metal has a density of 10.2 and melts at about  $2620^\circ$ . It can be drawn out into fine wire, and this is used as a support for the tungsten wire in electric lamps. The alloy *ferromolybdenum* is used in the preparation of molybdenum steel, which is especially well adapted to high-speed lathe tools and gun barrels. During the war the production of molybdenum from low-grade sulfide ores found in the state of Washington was greatly increased by the application of the "flotation process" for concentrating ores (p. 552).

Compounds of molybdenum are used for blue colors in porcelain painting, in coloring leather, for dyeing, and in chemical analysis.

**Tungsten.** For the most part tungsten occurs in nature as salts of tungstic acid ( $\text{H}_2\text{WO}_4$ ), especially as *scheelite* ( $\text{CaWO}_4$ ) and *wolframite* ( $\text{FeWO}_4$ ). Large quantities are produced annually, especially in China, Colorado, and Bolivia.

It is not difficult to produce the metal from the oxide as a fine powder, but it melts only at about  $3370^\circ$ , and it has been a brilliant achievement of chemical science to secure it in compact form and spin it out into very fine wire (0.3 mm.)

for use in electric lamps (Fig. 232). These lamps are about three times as efficient as the older carbon lamps. Because of its very high melting point the metal finds a wide use in electrical equipment at points where high temperatures are necessary, such as spark plugs in automobiles, switch-board contacts, and electric lamps. *Ferrotungsten* is employed in making tungsten steel, which is especially valuable for lathe tools, since it holds its temper at a red heat. The compounds of tungsten are relatively unimportant.

**Uranium.** Uranium is a rare element which is found chiefly as the oxide  $\text{U}_3\text{O}_8$  called *pitchblende*, or as the complex mineral *carnotite* ( $\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ ). These minerals are found most abundantly in Colorado and Utah, in the Belgian Congo, and in Russia.

Uranium forms many oxysalts such as uranyl nitrate ( $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and uranyl acetate ( $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ ). It also forms diuranates such as  $\text{Na}_2\text{U}_2\text{O}_7$ , analogous to the dichromate  $\text{Na}_2\text{Cr}_2\text{O}_7$ . Most of these compounds are yellow or red. Their chief use is in making greenish-yellow fluorescent glass, in china painting, and in making orange-colored pigments. Uranium steel has many superior qualities similar to those of tungsten steel.

The chief interest attached to uranium is that it has the highest atomic weight of all the elements, and that it is the source of *radium*, as will be described in the following chapter.

### VANADIUM, COLUMBIUM, AND TANTALUM

The three elements vanadium, columbium, and tantalum are pentavalent elements in group V in the periodic table. They are all three metallo-acid elements and form acids with formulas similar to those of the acids of phosphorus. They have very high melting points and high densities, and are very ductile.

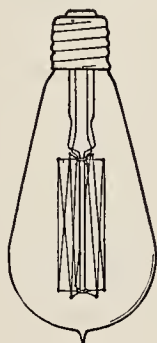


FIG. 232. A tungsten lamp



**Vanadium.** This element occurs most abundantly as a sulfide in Peru. It resembles chromium in many respects, forming salts that are green, blue, or violet in color and acids that are yellow or red. It passes from one stage of valence to another with ease, and so gives rise to many reactions of oxidation and reduction, attended by marked color changes. When its oxide is reduced along with iron oxide, the alloy *ferrovanadium* is obtained, which is extensively used in the production of vanadium steel, used in automobile construction. The vanadium plays the part of a purifier rather than that of an alloy metal. Compounds of vanadium are used as catalytic reagents and as photographic developers.

**Columbium and tantalum.** These elements are nearly always pentavalent and always play the part of acid-forming elements. Next to tungsten, tantalum has the highest melting point of all the metals ( $2850^{\circ}$ ), and it is one of the heaviest of metals, having a density of 16.6. For a time it was used in making electric lamps, but was soon replaced by tungsten. It may possibly replace platinum for a number of purposes, but unfortunately it oxidizes too readily to find a large use for laboratory utensils.

### EXERCISES

1. What elements are both acid-forming and base-forming?
2. Distinguish between oxidation and reduction in the broad sense of the terms.
3. For what purposes is manganese dioxide used?
4. Starting with pyrolusite, how could you prepare the following compounds: manganous chloride, manganous sulfate, manganous sulfide, potassium manganate, potassium permanganate?
5. Starting with chromium, how could you prepare the following compounds: chromous chloride, chromic sulfate, chrome alum?
6. How can you convert potassium chromate into potassium dichromate and vice versa?
7. Write the equation showing how ferrous sulfate can be oxidized to ferric sulfate by potassium dichromate in the presence of sulfuric acid.
8. A cleaning fluid commonly used in the laboratory for cleaning glassware consists of a mixture of sodium dichromate and commercial sulfuric acid. Wherein does its efficiency lie?

9. A simple method for preparing chlorine consists in adding hydrochloric acid, drop by drop, to potassium permanganate. Give the changes involved.

10. Which has the greater oxidizing value (*a*) 100 g. of potassium dichromate or (*b*) 100 g. of sodium dichromate?

11. (*a*) What is the percentage of manganese in pyrolusite? (*b*) of chromium in chrome iron ore?

12. What weight of pyrolusite is necessary for the preparation of 1 kg. of potassium permanganate.

13. What percentage of the total amount of oxygen present in potassium permanganate is available for oxidation?

14. What weight of ferrochromium containing 40 per cent of chromium must be added to a ton of steel to produce an alloy containing 3 per cent of chromium?

15. A sample of an iron ore weighing 0.2 g. was dissolved in sulfuric acid and the resulting ferrous sulfate oxidized to ferric sulfate by potassium permanganate. Assuming that 20 cc. of a solution of potassium permanganate, prepared by dissolving 3.16 g. of the permanganate in 1 liter of water, was required in order to oxidize the iron, what percentage of iron was present in the ore?

## CHAPTER XLIII

### RADIOACTIVITY ; RADIUM ; RADIOACTIVE ELEMENTS

**Introduction.** In the year 1896 the French physicist Becquerel (Fig. 238) carried out an experiment, very simple in itself and giving promise of no results of any unusual significance or practical value, the outcome of which, in its far-reaching importance, has probably never been surpassed in the history of science. It constituted the beginning of a remarkable series of discoveries that have changed our whole conception of the nature of electricity and the structure of the atom. This chapter will be devoted to a brief sketch of this remarkable story.

**X Rays.** In 1895 the German physicist Roentgen (Fig. 236) discovered that a Crookes vacuum tube is the source of a wonderful form of *radiation*, which he called X rays and which are sometimes called Roentgen rays. These rays, while stopped by metals like lead, are able to pass through all materials of small density and to act upon a photographic plate just as light does. The real source of these rays is the electrical energy that is used to excite the tube.

**Radioactivity.** The next year (1896) it occurred to Becquerel (Fig. 238) that similar radiations might be given off by those substances that are phosphorescent in the dark, and that this is the cause of their phosphorescence. Among other phosphorescent substances he tried some compounds of the rare metal *uranium*, wrapping them in black paper to exclude light and placing them on a photographic plate. He found that the plate was acted upon by these compounds in the same way as light acts upon it. The uranium compounds must therefore give off some sort of radiations, and these must differ from

light at least in their power to penetrate the black paper wrapped about the plate. Two facts of great importance were soon discovered:

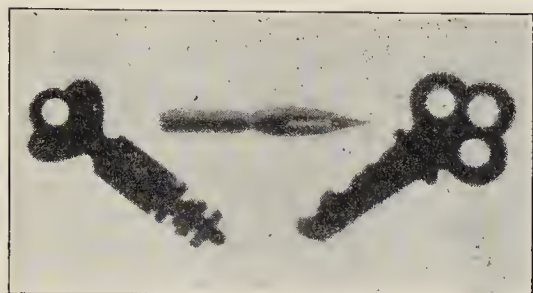


FIG. 233. A radiograph made by uranium radiations

(1) these rays could not pass through metal objects, so that radiographs could be made with them just as with X rays (Fig. 233); (2) when brought near these uranium compounds a charged electroscope was rapidly discharged (Fig. 235), showing that the air all around them was an *electrical conductor*, which is not true of ordinary air. The property that caused these effects was called *radioactivity*.

**Electroscope.** Fig. 234 represents a simple form of aluminum-leaf electroscope, the leaves spreading apart (indicated at *B*) when an electric charge is communicated to the knob *A*. When a substance containing uranium (Fig. 235, *C*) is brought near the knob, the charge is rapidly lost and the leaves collapse, as shown at *B*.

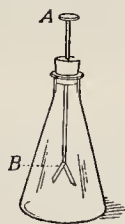


FIG. 234. A charged electroscope

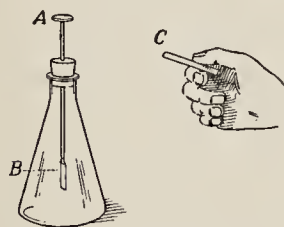


FIG. 235. An electroscope discharged by uranium radiations

**Work of the Curies.** At the suggestion of Becquerel, his associate Pierre Curie and his Polish bride, Madame Curie (Fig. 237), took up the problem of radioactivity. They found that the mineral *pitchblende* ( $\text{U}_3\text{O}_8$ ), the ore of uranium best known at that time, was *four times* as active as pure uranium oxide of the same formula prepared in

the laboratory, and they argued that there must be present in pitchblende a radioactive substance that is largely but not





FIG. 236. Wilhelm Konrad  
Roentgen (1845-1923)

A German physicist known especially for his discovery of X rays. This discovery was made in 1895 while he was professor of physics in the University of Würzburg. He was awarded the Nobel prize in 1901. He was also the recipient of many other honors, both in the United States and in Europe



FIG. 237. Madame Marie  
Curie (1867- )

Born in Warsaw, Poland. Now professor in the Sorbonne, Paris. Madame Curie, together with her husband, Pierre Curie, discovered polonium in July, 1898, and radium in December, 1898. Later she isolated pure radium, studied its properties, and determined its atomic weight. The Nobel prize was awarded to Monsieur and Madame Curie and Becquerel conjointly in 1903, and to Madame Curie alone in 1911. Elected honorary member of the American Chemical Society in 1909

FIG. 238. Henri Becquerel  
(1852-1908)

Late professor of physics in the Laboratory of the National Museum of Natural History in Paris. In 1896 he discovered that radiographs could be produced by uranium salts similar to those produced by X rays. It was this discovery that suggested to Monsieur and Madame Curie the investigations that later led to the discovery of polonium and radium

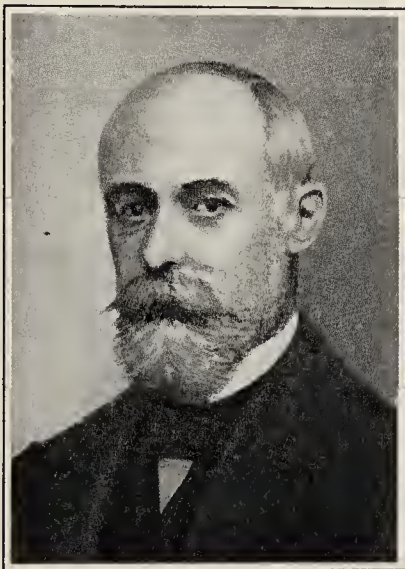
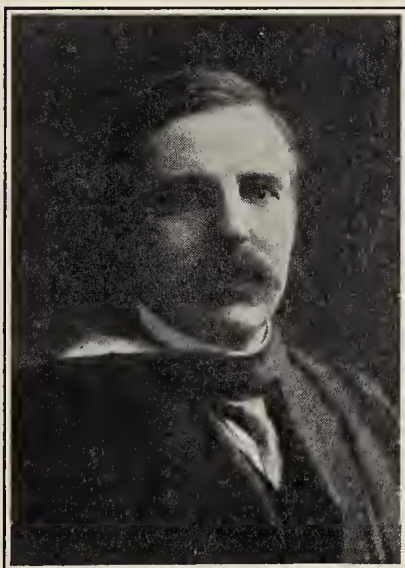


FIG. 239. Sir Ernest  
Rutherford  
(1870- )

Celebrated English physicist; director of the Cavendish laboratory at Cambridge; recipient of the Nobel prize for physics, in 1908, for his work on radioactivity and the structure of the atom



entirely removed in the process of purification. By long-continued work on residues obtained from tons of ore they finally isolated a minute quantity of the chloride of a new element which was one million times as radioactive as uranium, and which they named *radium*.

In 1906 Monsieur Curie was killed in a street accident, and Madame Curie continued the work, in which many others



FIG. 240. Picture taken in the laboratory of the Standard Chemical Company, showing the crystallization of the radium bromide which the women of America presented to Madame Curie on the occasion of her visit to America in 1921

now engaged. She found the atomic weight of radium to be 226, and this weight, as well as all the properties of the compounds of radium, placed the element below barium in the calcium family, in a place there vacant. A minute quantity of the metal was isolated in 1910 by Madame Curie.

In the spring of 1921 Madame Curie, then professor of physics at the University of Paris, paid a visit to the United States that attracted much attention in the daily press. Many honors were bestowed upon her by universities and scientific societies. By popular subscription the women of our country raised the sum of \$120,000, with which was purchased *1 gram* of radium in the form of radium bromide (Fig. 240) and on their behalf this was presented to Madame Curie by the president of the United States in the White House at Washington.

**Quantity of radium available.** In all other instances, when a new and very interesting element has been found, energetic search has soon provided a supply. This was not so with

radium. It was soon found that radium occurs in all *uranium ores and in no others*. It is a still more surprising fact that in all these ores the *ratio between the uranium and the radium is constant*, being about 1 part of radium to 3,400,000 parts of uranium. There is no hope of finding any other ores of radium save as we find new sources of uranium, and uranium ores are very rare.

The older source was pitchblende, occurring chiefly in Austria. A more abundant source is the rare mineral *carnotite*, found in the deserts of Colorado and Utah. This mineral has the complex composition expressed by the formula  $\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ . Until 1922 this was the chief source of radium. Up to that time the world's total production had amounted to less than 200 grams, of which the United States had produced about four fifths. It takes about 500 tons of carnotite to produce 1 gram of radium, and the value was \$120,000 for each gram of radium in the salt.

In 1922 a new source of uranium was discovered in the Belgian Congo; this is much richer in uranium than is carnotite, and can be mined and shipped at a much lower cost. This source has supplanted all others, and the price of radium has dropped to about \$70,000 per gram of radium content.

**Disintegration of radium.** As one looks casually at a sample of a radium salt, such as the chloride, there is little to distinguish it from any other white salt, such as its first cousin, barium chloride. But if we could watch many millions of radium *atoms* we should see a wonderful sight. Every now and then we should see one of these atoms explode violently (much as now and then a grain of pop corn explodes as we warm the corn), and it then ceases to be a radium atom. The rate at which these explosions take place makes the *average* age of a radium atom about twenty-five hundred years. As a result of these explosions all compounds of radium are constantly giving off three kinds of so-called rays. These are designated as *alpha rays*, *beta rays*, and *gamma rays*.



**Nature of the rays.** A gram of radium shoots off *every second*, at a velocity of about 12,000 miles per second, 145 *billion* particles that are the alpha rays. They consist of *positively charged* helium atoms. At the same time 71,000 *billion* particles, constituting the beta rays, are shot off, and these have a velocity of about ten times that of the alpha rays. They are *negatively charged*, and in mass are about  $\frac{1}{1845}$  as heavy as hydrogen atoms. *They constitute the electrons which are present in the atoms of all the elements* (p. 265). The gamma rays are not made up of matter, but are vibrations in the ether, just as light is. They correspond to the flash of light that often accompanies an ordinary explosion, and move with the same velocity as light, but they differ from light in having very short wave lengths, as X rays have. The rate of these explosions is kept up very steadily all the time and is not changed by any means yet tried (such as very high or very low temperatures), and all compounds of radium act just alike in the rate of these explosions.

**The detection and estimation of radium.** When any material containing radium is brought near to the knob of a charged electroscope (Fig. 234), the charged particles in the air, coming into contact with the knob, very rapidly discharge the electroscope, as is evidenced by the falling together of the aluminum leaves. The rate at which this takes place can be used to estimate, with extraordinary precision, the quantity of radium present. Soddy has estimated that if half a grain of radium bromide (0.0328 g.) were to be divided equally among all the human beings in the world, one such portion could be detected.

**Demonstration of the three types of rays.** The existence of three different types of rays can be demonstrated in the following way: A small quantity of material rich in radium is placed at the bottom of a hole bored in a piece of lead (*A*, Fig. 241). A photographic plate *B*, protected from light, is fixed at some distance above the radium, and a magnetic field is applied at right angles to the plane of the paper so that the lines of magnetic force travel

downward into the plane. Under these conditions both the alpha and the beta rays emitted by the radium are deflected from their course, but in opposite direction and to different degrees, as shown in Fig. 241. The gamma rays are not deflected at all. By developing the photographic plate the extent of deflection of the alpha and beta rays can be measured, and from such measurements it is possible to arrive at conclusions as to the relative masses and charges of the two kinds of particles.

### Where radium comes from.

Radium is decomposing at a rate that puts its average age at approximately 2500 years, and yet the rocks in

which it is found are very much older than this. Why has any radium survived? Plainly it must be in constant process of formation from some other element, and it has been proved that this parent element is *uranium*. Uranium is also going to pieces (it is radioactive), *but at a much slower rate than radium*. So all uranium ores must contain radium, and none can contain very much. The quantity of radium present is merely the result of equilibrium between the rate of formation and the rate of disintegration. So we see why we shall never find rich radium ores. If anyone were to find such an ore, we should have to change all our ideas about radium.

**Internal energy of radium.** If the explosions of the radium atoms are as terrific as we have pictured them, and if the alpha and beta rays are shot off with such incredible velocities, the energy set free must be much greater than that of any known reaction between elements. The radium compound actually keeps warm all the time. It is estimated that 1 g. of radium evolves 135 cal. of heat *hourly*, and this is kept up for the average life of twenty-five hundred years. From this it can be computed that the total energy given off by a gram of

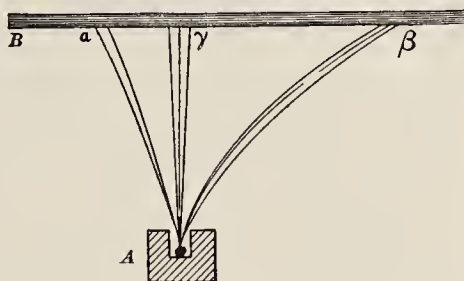


FIG. 241. Three types of rays emitted by radioactive substances, separated by the action of a magnet

radium in disintegrating into lead is about 250,000 times the heat of combustion of 1 gram of the element carbon.

**Practical uses of radium.** Such a remarkable material as radium could hardly fail to find useful applications. The rays emitted from radium, particularly the gamma rays, produce many chemical and physiological effects. They disintegrate glass, water, and many other substances. They render certain materials luminous in the dark, and enamel paints containing radium are used to illumine the hands of watches, the push buttons of electric lights, and the keyholes of doors. They produce severe burns upon the skin like those of X rays. They kill bacteria and other microorganisms.

The latter property has led to the hope that exposure to the radiations of radium compounds might, under proper conditions, prove to be of service in effecting a cure for some diseases of the skin and for cancer. It is not possible to say as yet to what extent these hopes will be realized. Certain forms of cancer have almost certainly been cured in this way, and the progress of other forms has been arrested.

**Uranium series of elements.** It must not be thought that an atom of radium or of uranium goes entirely to pieces, forming nothing but alpha and beta rays, when it explodes. The loss of one of these rays by a uranium atom creates a new atom, which by a fresh explosion gives rise in turn to still another atom. This process continues until, finally, an atom is formed which does not explode, and all radioactivity then ceases. *This final element is lead.* There are in this series thirteen radioactive elements between uranium and lead, radium being the fifth. The immediate product of radium is the gaseous element *radon* (it was formerly called *niton*), and its explosion is the most terrific of the whole series.

Radon is the most effective of the radioactive elements for medical purposes, partly because of the intense energy of its explosion and partly because it can be measured out in thin glass tubes and applied very directly to a limited locality. It has been

proposed to sell these standardized tubes to the medical profession, rather than the extremely costly radium itself. The following table gives the chief items of interest in regard to the radioactive elements derived from uranium.

TABLE OF URANIUM SERIES

NAME	SYMBOL	ATOMIC WEIGHT	ATOMIC NUMBER	ISOTOPE	RADIATION	AVERAGE LIFE
Uranium I . . .	UI	238	92	U	$\alpha$	$6.75 \times 10^9$ yr.
Uranium $X_1$ . .	UX <sub>1</sub>	234	90	Th	$\beta$	35.5 da.
Uranium $X_2$ . .	UX <sub>2</sub>	234	91	Pa	$\beta$	1.65 min.
Uranium II . . .	UII	234	92	U	$\alpha$	$3 \times 10^6$ yr.
Ionium . . . . .	Io	230	90	Th	$\alpha$	$10^5$ yr.
Radium . . . . .	Ra	226	88	Ra	$\alpha$ ( $\beta$ )	2440 yr.
Radon (niton) . .	Rn	222	86	Rn	$\alpha$	5.55 da.
Radium A . . .	RaA	218	84	Po	$\alpha$	4.32 min.
Radium B . . .	RaB	214	82	Pb	$\beta$	38.7 min.
Radium C . . .	RaC	214	83	Bi	$\beta$	28.1 min.
Radium C' . . .	RaC'	214	84	Po	$\alpha$	$10^{-6}$ sec.
Radium D . . .	RaD	210	82	Pb	$\beta$	23.8 yr.
Radium E . . .	RaE	210	83	Bi	$\beta$	7.2 da.
Radium F . . .	RaF	210	84	Po	$\alpha$	196 da.
Radium $\Omega'$ (lead)	Ra $\Omega'$	206	82	Pb		

**Radioactive elements and the periodic law.** An inspection of the periodic table will show that as we pass from one group to the next the elements increase in valence by one, which means that they *gain one positive charge or lose a negative one*. Thus, the sodium ion is  $\text{Na}^+$  and the calcium ion is  $\text{Ca}^{++}$ .

When a uranium atom having the atomic weight 238.1 loses a helium atom having the atomic weight 4 and carrying two positive charges, the product ( $\text{UX}_1$ ) should have an atomic weight of 234.1 and should find a place in Group IV. But this place is already occupied by thorium (atomic weight, 232.12). Similarly, when  $\text{UX}_1$  loses an electron (one negative charge but no appreciable weight), the new element so formed ( $\text{UX}_2$ ) should have a place in Group V, where there happens to be a vacancy.



**Radioactive isotopes.** If we trace in this way the thirteen elements between uranium and lead, we shall find that they usually fall into places already occupied by other elements, most of which are not radioactive, and which in general have atomic weights differing from those of the radioactive elements. If we examine the two elements, we find that they have identical chemical properties, and when they are mixed they cannot be separated by chemical methods. Such a pair of elements are called *radioactive isotopes*, to distinguish them from the class of isotopes that we have already studied (p. 272).

**Lead derived from uranium.** Between uranium and lead 8 alpha rays (charged helium atoms) have been successively shot off, making a total of 32 atomic units. Subtracting this from 238.1 (the atomic weight of uranium), we get 206.1 for the atomic weight of lead. The atomic weight of ordinary lead is 207.2. Richards made a very careful determination of the atomic weight of lead obtained from uranium ores and found it to be 206.06. The lead derived from uranium is therefore an isotope of ordinary lead.

**Other radioactive series.** The well-known element thorium resembles uranium closely in being radioactive and in giving rise to a long series of radioactive elements. The end product of this series is also an isotope of lead with an atomic weight of about 208.

A third element, *actinium*, is apparently derived from uranium in one of its first decomposition stages, and in turn gives rise to a third series of radioactive elements. Both potassium and rubidium appear to have slight radioactivity, but nothing is known about their products.

**Atomic systems.** Much knowledge of the structure of the atom has been gained through the study of the effects produced upon ordinary atoms by the bombardment of the alpha and beta rays from radioactive elements, with their enormous velocities. It seems certain that the nucleus of all atoms is composed of charged helium, or of charged helium and charged

hydrogen, together with electrons. About this nucleus a limited number of electrons are spaced like the planets about the sun; and the *volume* of the whole atom is marked out by the position of these outer electrons, just as the volume of our solar system may be said to be the volume included in the orbit of Neptune. In fact, the *relative* magnitudes in the atom and in the solar system are roughly parallel, the sun, the planets, and their distances apart corresponding to the nucleus, the outer electrons, and their distances apart. Alpha rays may therefore pass right through an atom without hitting anything, just as a comet may pass through our solar system without colliding with any member of the system. In fact, the rays are so minute in comparison to the size of the atom as fixed by the orbit of its outermost electron that only very rarely should we expect a collision to take place. If a collision does occur, one or more electrons may be knocked away from the atom, thus forming the atom of some other element. It will be recalled that in this way Rutherford succeeded in decomposing a number of elements (p. 272).

#### EXERCISES

1. When was uranium discovered, and how did it get its name? (See encyclopedia.)
2. For whom was carnotite named? (See dictionary.)
3. How is an electroscope charged? (See physics.)
4. What is the meaning of *alpha*, *beta*, and *gamma*?
5. The velocity of light is, in round numbers, 186,000 miles, or 300,000 kilometers per second (in a vacuum). Compare the velocity of the alpha, beta, and gamma rays shot off by radium with the velocity of light.
6. How did thorium get its name? For what is the element used?
7. Would it necessarily be true that all lead was once uranium?
8. The fastest-moving projectiles from a cannon (the German big berthas that bombarded Paris) move a mile a second. How does the velocity of the alpha ray compare with this?

## CHAPTER XLIV

### GOLD AND THE PLATINUM METALS

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	HIGHEST OXIDE	HIGHEST CHLORIDE	MELTING POINT
Ruthenium . .	Ru	101.7	12.2	$\text{RuO}_4$	$\text{RuCl}_4$	2450° (?)
Rhodium . . .	Rh	102.9	12.5	$\text{RhO}_2$	$\text{RhCl}_3$	1955°
Palladium . . .	Pd	106.7	12.0	$\text{PdO}_2$	$\text{PdCl}_4$	1555°
Iridium . . . .	Ir	193.1	22.4	$\text{IrO}_2$	$\text{IrCl}_4$	2350° (?)
Osmium . . . .	Os	190.8	22.48	$\text{OsO}_4$	$\text{OsCl}_4$	2700° (?)
Platinum . . . .	Pt	195.2	21.45	$\text{PtO}_2$	$\text{PtCl}_4$	1755°
Gold . . . . .	Au	197.2	19.3	$\text{Au}_2\text{O}_3$	$\text{AuCl}_3$	1063°

**The family.** Following iron, cobalt, and nickel in the eighth column of the periodic table are two groups of three elements each. The metals of the first of these groups — ruthenium, rhodium, and palladium — have atomic weights near 100 and densities near 12. The metals of the other group — iridium, osmium, and platinum — have atomic weights near 200 and densities near 21. These six rare elements have very similar physical properties and resemble each other chemically not only in the type of compounds which they form but also in the great variety of them. They occur closely associated in nature, usually as alloys of platinum in the form of irregular metallic grains in sand and gravel. They are known collectively as the platinum metals. Platinum and palladium are by far the most abundant of the six.

Although the periodic classification assigns gold to the silver-copper group, it much more closely resembles the platinum metals in its physical properties as well as in its chemical conduct, and it can be conveniently considered along with

them. All these metals are below hydrogen in the electro-chemical series and are consequently inactive toward acids. The four elements gold, platinum, osmium, and iridium are the heaviest substances known, being about twice as heavy as lead.

## GOLD

**Occurrence.** From the earliest times gold has been known as a precious metal. It was called *aurum* by the Romans, and from this name the symbol Au is derived. For the most part it is found in nature in the native state, either embedded in quartz veins or as grains or large nuggets in the heavy sands derived from them. In this state it is usually alloyed with smaller quantities of other metals, such as silver, copper, and lead. In combination it occurs as a constituent of a number of minerals, nearly all of which contain tellurium, together with silver and some copper. In the past few years the gold production of the world has amounted to about \$340,000,000 annually. Of this amount South Africa (principally the Transvaal and Rhodesia) produces over one half. The United States comes next, producing about 15 per cent of the world's supply. Gold is the basis of international credit, and its price is fixed at \$20.67 per troy ounce.

**Mining and extraction.** Native gold is obtained in crude form by *placer* mining. The sand containing the gold is shaken or stirred in troughs of running water, called *sluices*. This sweeps away the sand but allows the heavier gold to sink to the bottom of the sluice. Sometimes the sand containing the gold is washed away from its natural location into the sluices by powerful streams of water delivered under pressure from pipes, as illustrated in Fig. 242. This method of obtaining gold is called *hydraulic* mining. In *vein* mining the gold-bearing quartz is stamped into fine powder in stamping mills, and the gold is extracted by a number of processes, two of which will be described.



1. *Amalgamation process.* In the amalgamation process the powder containing the gold is washed over a series of copper plates whose surfaces have been amalgamated with mercury. The gold sticks to the mercury or alloys with it, and after a time the gold and mercury are scraped off and the mixture is distilled. The mercury distills off, and the gold is left in the retort ready for refining.



FIG. 242. Hydraulic mining of gold

2. *Cyanide process.* This process depends upon the fact that gold is soluble in a solution of sodium cyanide in the presence of the oxygen of the air. The powder from the stamping mills is treated with a very dilute sodium cyanide solution which extracts the gold. From this solution the gold can be obtained by electrolysis or by precipitation with metallic zinc.

**Refining of gold.** Gold is refined by three general methods:

1. *Electrolysis.* When gold is dissolved in a solution of sodium cyanide and the solution is electrolyzed, the gold is deposited in very pure condition on the cathode.

2. *Cupellation.* When the gold is alloyed with easily oxidizable metals, such as copper or lead, it may be refined by cupellation. The alloy is fused with an oxidizing flame on a shallow hearth made of bone ash, which has the property of absorbing metallic oxides but not the gold. Any silver which may be present remains alloyed with the gold.

3. *Parting with sulfuric acid.* Gold may be separated from silver, as well as from many other metals, by heating the alloy with concentrated sulfuric acid. This dissolves the silver, while the gold is not attacked. Sometimes nitric acid is used instead of sulfuric acid.

**Properties.** Gold is a yellow metal of density 19.3. It melts at about the same temperature as copper ( $1063^{\circ}$ ) and boils at approximately  $2600^{\circ}$ . It is about as soft as silver, is a good conductor of electricity, and is the most ductile and malleable of all the metals. Its extreme malleability may be inferred from the fact that 1 g. of gold will make 800 sq. in. of ordinary gold leaf. It forms alloys with most of the metals, and its uses are too familiar to require description. In a pure condition gold is too soft to be used for jewelry and coinage, and for such purposes it is always alloyed with copper or silver. The fineness of gold is usually expressed in terms of carats, 24-carat gold being pure, while 18-carat (75 per cent) is the grade used for the best jewelry. For coinage a 90 per cent alloy is used. The finest ruby-colored glass is produced by the addition of a little metallic gold, the color being due to the presence of gold in colloidal dispersion.

**Chemical conduct.** Gold is not attacked by any of the common acids; aqua regia easily dissolves it, forming *chlorauric acid* ( $\text{HAuCl}_4$ ). Fused alkalis also attack it. Most oxidizing agents are without action upon it, and in general it is not an active element.

**Compounds.** The compounds of gold, though numerous and varied in character, are of comparatively little importance and need not be described in detail. The element forms two series of salts in which it acts as a metal: in the aurous series the gold is univalent, the chloride having the formula  $\text{AuCl}$ ; in the auric series

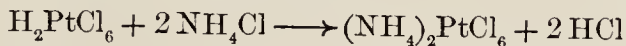
it is tervalent, auric chloride having the formula  $\text{AuCl}_3$ . Gold also acts as an acid-forming element, as shown in such compounds as potassium aurate ( $\text{KAuO}_2$ ). Its compounds are very easily decomposed, however, with the separation of metallic gold.

## PLATINUM

**History and occurrence.** The element *platinum* owes its name to the Spanish word *platina*, which is a diminutive of the word *plata*, meaning "silver." It was first described with some care by Brownrigg in 1750. Platinum occurs in nature alloyed with various other metals belonging to the gold and platinum families, as well as with copper and iron. It is found chiefly in the Ural Mountains in Russia, smaller quantities being found in Brazil, Colombia, and the Pacific coast states. At present, with Russia out of the running, Colombia is furnishing most of the platinum. The entire production, however, is only a small percentage of the pre-war production. Like gold, it occurs in heavy sands, associated with magnetite, rutile, diamond, and quartz, and constitutes from 50 to 80 per cent of the crude alloy. A single well-defined mineral compound is known; namely, *sperrylite* ( $\text{PtAs}_2$ ). Some platinum is now recovered from the electrolytic mud of the gold and silver refineries.

In normal times Russia furnishes by far the largest amount of the metal. Thus, in 1914 that country produced 241,200 troy ounces out of a total world's production of 263,453. During the World War this supply was cut off, while at the same time the demand for platinum, especially for use as a catalyzer in the production of sulfuric acid and other chemicals, greatly increased. As a result the price of the metal rose from about \$45 per troy ounce in 1914 to \$105 in 1918. Because of the importance of the metal for war purposes, and because of its limited supply, the government restricted its use and at the same time purchased a considerable supply. At the close of the war the government sold its excess supply at \$105 per troy ounce, which is five times the price of gold. Since the war the price has greatly decreased, but it is still above that of gold.

**Preparation.** To separate the platinum from the alloy in which it is found in nature, the alloy is dissolved in aqua regia, which converts the platinum into chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ). Ammonium chloride is then added, which precipitates the platinum as insoluble ammonium chloroplatinate;



Some iridium is also precipitated as a similar compound. On ignition the double chloride is decomposed, leaving the platinum as a spongy metallic mass, which is melted in an electric furnace and rolled or hammered into the desired shape.

**Properties and chemical conduct.** Platinum is a grayish-white metal of density 21.45, which melts at  $1755^\circ$ . It is very malleable and ductile. Platinum has been drawn out into a wire so fine that a cube of the metal, each side of which is 2 cm. long, would furnish sufficient wire to girdle the earth two and one-half times. It is harder than gold and is a good conductor of electricity. In finely divided form it adsorbs gases, especially oxygen and hydrogen. Under these conditions the gases are very active and will combine with each other at ordinary temperatures. Thus, a jet of hydrogen or coal gas directed upon spongy platinum is at once ignited. Under ordinary conditions it is not attacked by the common acids, though hot concentrated sulfuric acid slowly dissolves it. It is quite permanent in the air, and neither oxygen nor water vapor attacks it even at red heat. Free chlorine dissolves it, forming platinum tetrachloride ( $\text{PtCl}_4$ ). Aqua regia converts it into *chloroplatinic acid* ( $\text{H}_2\text{PtCl}_6$ ). Fused alkalis corrode it, forming platينات, especially in the presence of oxidizing agents such as nitrates. It alloys readily with many easily reducible metals and is therefore attacked or dissolved when heated with compounds of such metals together with a reducing agent.

**Platinum as a catalytic agent.** Platinum is remarkable for its property of acting as a catalytic agent in a large number of chemical reactions, and mention has been made of this use of the metal



in connection with the manufacture of sulfuric acid and nitric acid. When desired for this purpose some porous or fibrous substance, such as asbestos, is soaked in a solution of chloroplatinic acid and then ignited. The platinum compound is decomposed and the platinum deposited in very finely divided form. Asbestos prepared in this way is called *platinized asbestos*. For some reactions, as in the oxidation of ammonia by air (p. 228), the platinum is used in the form of a finely woven gauze. The catalytic action seems to be in part connected with the property of adsorbing gases and rendering them nascent. Some other metals possess this same power, notably palladium, which is remarkable for its ability to adsorb hydrogen.



FIG. 243. Some laboratory utensils made of platinum

**Applications.** The applications of platinum in the sciences and the industries depend largely upon its high melting point, its chemical inactivity, and its malleability and ductility. It is extensively used (1) in scientific laboratories and in certain industries for evaporating pans, catalytic materials, and a great variety of laboratory appliances (Fig. 243); (2) in electrical apparatus for contact points; (3) in dentistry as pins for artificial teeth and as foil and plates in construction work; and (4) in jewelry as a substitute for gold. Because of the limited supply of the metal and its fundamental importance in necessary industries, it is unfortunate and unreasonable that it should be used for jewelry.

The following rough estimate has been made of the amount of platinum produced and of its uses: "Of the 5,000,000 or more

ounces of platinum in existence, catalyzing processes have claimed 500,000 oz.; dental uses, 1,000,000 oz.; chemical apparatus, 1,000,000 oz.; electrical devices, 500,000 oz.; and jewelry, 500,000 oz."

**Platinum substitutes.** To meet the serious shortage of platinum, efforts are being made to discourage its use in jewelry and to provide substitutes for other uses. Tungsten is taking its place for many purposes, especially for electrical spark contacts; wires of nickel iron coated with copper are now used in the manufacture of incandescent lamps; electrical-resistance heaters are made of alloys of nickel and chromium; quartz dishes are substituted for platinum in the industries; and a variety of alloys are being proposed for use in small laboratory utensils. Among these the following are the most promising at present:

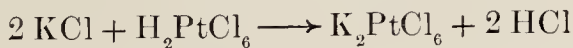
Palau, an alloy of palladium (Pal) and gold (Au)

Rhotanium, an alloy of gold, palladium, and a small percentage of rhodium

Illium, essentially an alloy of nickel, chromium, copper, and molybdenum

**Compounds.** Platinum forms two series of salts, of which platinous chloride ( $\text{PtCl}_2$ ) and platinic chloride ( $\text{PtCl}_4$ ) are examples. Platinates are also known. While a great variety of compounds of platinum have been made, the substance is chiefly employed in the metallic state.

**Chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ).** When platinum is dissolved in aqua regia and the solution is crystallized, brownish-red crystals of the hydrate of chloroplatinic acid are obtained of the composition  $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$ . The potassium and ammonium salts of this acid are nearly insoluble in water and alcohol. The acid is therefore used as a reagent to precipitate potassium in analytical work. With potassium chloride the equation is



**Other metals of the family.** Of the other members of the family, *palladium* is the most abundant. Alloyed with platinum it occurs in considerable quantities in Brazil. It is also present in minute quantities in many ores of copper and nickel, and at present the chief source of palladium is the electrolytic muds of the nickel refineries.

Palladium is only about half as heavy as platinum, melts much lower, and is harder. It is used as a solder for platinum, for making graduated scales in scientific instruments, for making alloys, and as a substitute for platinum in jewelry. In the form of a powder it is a remarkably active catalytic agent; 1 volume of the finely divided metal adsorbs 800 volumes of hydrogen.

*Iridium* gives a very hard alloy with platinum, used for fountain pen points, compass bearings, and standard weights and measures.

*Osmium tetroxide* ( $\text{OsO}_4$ ) is a very volatile liquid and is used under the name of *osmic acid* as a stain for sections in microscopy.

#### EXERCISES

1. From the method of preparation of platinum, what metal is likely to be alloyed with it?
2. The "platinum chloride" of the laboratory is made by dissolving platinum in aqua regia. What is the compound?
3. How do we expect potassium aurate and platinate to be formed?
4. Why cannot laboratory vessels be made of gold instead of platinum?
5. What uses of platinum would seem to lose it permanently?
6. If platinum and palladium cost the same per ounce, which would be the more economical to use for jewelry?
7. What weight of gold would be necessary to make 1 square meter of gold leaf?
8. Suggest precautions that should be taken in using a platinum crucible for laboratory purposes.
9. What weight of chlorauric acid can be prepared from 5 g. of 18-carat gold?
10. A piece of pure platinum foil weighing 3 g. was dissolved in aqua regia, and the solution was evaporated to dryness. Calculate the weight of the residue.
11. Ammonium chloroplatinate is reduced to metallic platinum on heating. What weight of the metal will 100 g. of the salt yield?

## APPENDIX

### CRYSTALLOGRAPHY

A crystal is always bounded by plane surfaces, arranged in an orderly fashion with reference to imaginary lines drawn through the crystal and called its axes. Every crystal has therefore a definite geometric form. While the variety of form which crystals may assume is almost endless, it has been found that they may all be referred to one of six fundamental arrangements of axes, these constituting what are known as the systems of crystallography. These arrangements, together with two of the simplest crystal forms referred to each, are shown in the accompanying figures (Figs. 244-250).

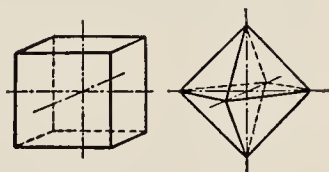


FIG. 244

**The crystal systems.** The relation of the axes in the several systems is as follows :

1. Isometric or regular system (Fig. 244) : three equal axes all at right angles to each other.
2. Tetragonal system (Fig. 245) : two equal axes and a third of different length, all at right angles.
3. Rhombic system (Fig. 246) : three unequal axes all at right angles.

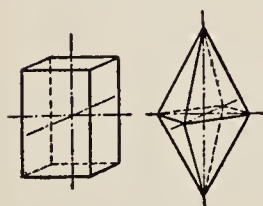


FIG. 245

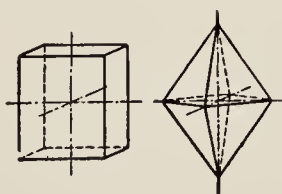


FIG. 246

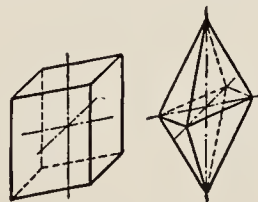


FIG. 247

4. Monoclinic system (Fig. 247) : two axes at right angles and a third at right angles to one of these but inclined toward the other. The axes may be of any relative lengths, and the angle of inclination may vary from  $0^\circ$  to  $90^\circ$ .



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5. Triclinic system (Fig. 248): three axes, all inclined toward each other. The axes may be of any relative lengths, and the angles of inclination may also vary.

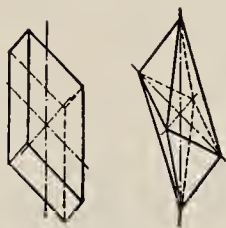


FIG. 248

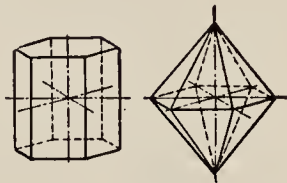


FIG. 249



FIG. 250

6. Hexagonal system (Fig. 249): three equal axes in the same plane, intersecting at angles of  $60^\circ$ , and a fourth at right angles to all of these. In addition to the two general forms shown in Fig. 249 there are many rhombic forms belonging to this system, such as the one represented in Fig. 250.

### DENSITIES AND MELTING POINTS OF SOME OF THE ELEMENTS

NAME	DENSITY	MELTING POINT	NAME	DENSITY	MELTING POINT
Aluminum . . .	2.70	$660^\circ$	Mercury . . . .	13.54	$-38.87^\circ$
Antimony . . .	6.68	$630.5^\circ$	Molybdenum . . .	10.2	$2620^\circ(?)$
Arsenic . . . .	5.7	sublimes	Nickel . . . . .	8.90	$1452^\circ$
Barium . . . .	3.5	$850^\circ$	Palladium . . . .	12.0	$1555^\circ$
Bismuth . . . .	9.80	$271^\circ$	Phosphorus (red) .	2.20	—
Boron . . . . .	$2.5(?)$	$2300^\circ(?)$	Phosphorus (yellow)	1.82	$44.1^\circ$
Bromine . . . .	3.11	$-7.2^\circ$	Platinum . . . .	21.45	$1755^\circ$
Cadmium . . . .	8.6	$320.9^\circ$	Potassium . . . .	0.86	$62.3^\circ$
Calcium . . . .	1.55	$810^\circ$	Radium . . . . .	5(?)	$960^\circ(?)$
Carbon (diamond)	3.51	—	Selenium . . . . .	4.80	$220^\circ$
Carbon (graphite)	2.25	$3500^\circ(?)$	Silicon . . . . .	2.4	$1420^\circ$
Chromium . . . .	7.1	$1615^\circ$	Silver . . . . .	$10.5(?)$	$960.5^\circ$
Cobalt . . . . .	8.9	$1480^\circ$	Sodium . . . . .	0.97	$97.5^\circ$
Copper . . . . .	8.92	$1083^\circ$	Strontium . . . .	2.6	$800^\circ(?)$
Gallium . . . .	5.91	$29.7^\circ$	Sulfur (monoclinic)	1.96	$119.0^\circ$
Gold . . . . .	19.3	$1063^\circ$	Sulfur (rhombic) .	2.07	$112.8^\circ$
Iodine . . . . .	4.93	$113.5^\circ$	Tantalum . . . .	16.6	$2850^\circ(?)$
Iridium . . . .	22.41	$2350^\circ(?)$	Tellurium . . . .	6.24	$452^\circ$
Iron . . . . .	7.86	$1535^\circ$	Tin . . . . .	7.31	$231.8^\circ$
Lead . . . . .	11.34	$327.5^\circ$	Titanium . . . .	4.5	$1800^\circ$
Lithium . . . .	0.53	$186^\circ$	Tungsten . . . .	19.3	$3370^\circ(?)$
Magnesium . . .	1.74	$651^\circ$	Vanadium . . . .	5.9	$1710^\circ(?)$
Manganese . . .	7.2	$1260^\circ$	Zinc . . . . .	7.14	$419.4^\circ$

## RELATION BETWEEN ENGLISH AND METRIC CONSTANTS

1 pound (troy) = 373.24 grams
1 ounce (troy) = 31.10348 grams
1 pound (avoirdupois) = 453.59 grams
1 ounce (avoirdupois) = 28.3495 grams
1 kilogram = 2.67923 pounds (troy)
1 kilogram = 2.20462 pounds (avoirdupois)
1 liter = 1.05668 United States quarts
1 gallon = 3.78543 liters
1 cubic centimeter = 0.0610 cubic inch
1 cubic inch = 16.3872 cubic centimeters
1 centimeter = 0.3937 inch
1 meter = 39.37 inches

One cubic centimeter of water at its temperature of greatest density (4° C.) weighs approximately 1 g. For all practical purposes, therefore, 1 cc. of water may be regarded as weighing 1 g.

## SOLUBILITY OF VARIOUS GASES IN WATER

NAME OF GAS	VOLUME ABSORBED AT 0° AND UNDER 760 MM. PRESSURE BY 1 LITER OF WATER
Ammonia . . . . .	1298.9 liters
Hydrogen chloride . . . . .	506.0 liters
Sulfur dioxide . . . . .	79.79 liters
Hydrogen sulfide . . . . .	4.37 liters
Carbon dioxide . . . . .	1.713 liters
Oxygen . . . . .	0.0489 liters
Nitrogen . . . . .	0.0233 liters
Hydrogen . . . . .	0.0214 liters

## TABLE OF SOLUBILITY OF VARIOUS SOLIDS

SUBSTANCE	FORMULA	WEIGHT DISSOLVED BY 100 CC. OF WATER AT		
		0°	20°	100°
Calcium chloride . . .	CaCl <sub>2</sub>	59.5 g.	74.5 g.	159.0 g.
Sodium chloride . . .	NaCl	35.70 g.	36.0 g.	39.80 g.
Potassium nitrate . .	KNO <sub>3</sub>	13.30 g.	31.6 g.	246.0 g.
Copper sulfate . . .	CuSO <sub>4</sub>	14.30 g.	21.7 g.	75.4 g.
Calcium sulfate . . .	CaSO <sub>4</sub>	0.759 g.	0.203 g.	0.162 g.
Calcium hydroxide . .	Ca(OH) <sub>2</sub>	0.185 g.	0.165 g.	0.077 g.

## TABLE OF ISOTOPES

NOTE. The table below gives the minimum number of isotopes and the atomic weight of each in the case of the more important elements. The elements are arranged in accordance with their atomic numbers.

NAME OF ELEMENT	ATOMIC NUMBER	ATOMIC WEIGHT	MINIMUM NUMBER OF ISOTOPES	ATOMIC WEIGHTS IN ORDER OF IMPORTANCE
Hydrogen . . .	1	1.008	1	1.008
Helium . . . .	2	4.002	1	4.00
Lithium . . . .	3	6.940	2	7, 6
Beryllium . . .	4	9.02	1	9
Boron . . . . .	5	10.82	2	11, 10
Carbon . . . . .	6	12.000	1	12
Nitrogen . . . .	7	14.008	1	14
Oxygen . . . . .	8	16.000	1	16
Fluorine . . . .	9	19.00	1	19
Neon . . . . .	10	20.183	2	20, 22
Magnesium . . .	12	24.32	3	24, 25, 26
Aluminum . . .	13	26.97	1	27
Silicon . . . . .	14	28.06	3	28, 29, 30
Phosphorus . .	15	31.02	1	31
Sulfur . . . . .	16	32.06	1	32
Chlorine . . . .	17	35.457	2	35, 37
Argon . . . . .	18	39.94	2	40, 36
Potassium . . .	19	39.10	2	39, 41
Calcium . . . .	20	40.07	2	40, 44
Iron . . . . .	26	55.84	2	56, 54
Nickel . . . . .	28	58.69	2	58, 60
Copper . . . . .	29	63.57	2	63, 65
Zinc . . . . .	30	65.38	4	64, 66, 68, 70
Selenium . . . .	34	79.2	6	80, 78, 76, 82, 77, 74
Bromine . . . .	35	79.916	2	79, 81
Krypton . . . .	36	82.9	6	84, 86, 82, 83, 80, 78
Rubidium . . . .	37	85.44	2	85, 87
Strontium . . . .	38	87.63	2	88, 86
Silver . . . . .	47	107.88	2	107, 109
Cadmium . . . .	48	112.41	6	110, 111, 112, 113, 114, 116
Tin . . . . .	50	118.70	7 (8)	120, 118, 116, 124, 119, 117, 122, (121?)
Antimony . . . .	51	121.76	2	121, 123
Tellurium . . . .	52	127.5	3	128, 130, 126
Xenon . . . . .	54	130.2	7 (9)	129, 132, 131, 134, 136, 128, 130, (126?), (124?)
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# TENSION OF AQUEOUS VAPOR EXPRESSED IN MILLIMETERS OF MERCURY

(Physical and Chemical Constants, Kaye and Laby)

TEMPERATURE	PRESSURE	TEMPERATURE	PRESSURE
10° . . . . .	9.20	26° . . . . .	25.13
11° . . . . .	9.84	27° . . . . .	26.65
12° . . . . .	10.51	28° . . . . .	28.25
13° . . . . .	11.23	29° . . . . .	29.94
14° . . . . .	11.98	30° . . . . .	31.74
15° . . . . .	12.78	31° . . . . .	33.57
16° . . . . .	13.62	32° . . . . .	35.53
17° . . . . .	14.52	33° . . . . .	37.59
18° . . . . .	15.46	34° . . . . .	39.75
19° . . . . .	16.56	35° . . . . .	42.02
20° . . . . .	17.51	36° . . . . .	44.40
21° . . . . .	18.62	37° . . . . .	46.90
22° . . . . .	19.79	38° . . . . .	49.51
23° . . . . .	21.02	40° . . . . .	55.13
24° . . . . .	22.32	50° . . . . .	92.30
25° . . . . .	23.69	100° . . . . .	760.00

## WEIGHT IN GRAMS OF 1 LITER OF VARIOUS GASES UNDER STANDARD CONDITIONS; BOILING POINTS UNDER PRESSURE OF 760 MILLIMETERS

NAME	WEIGHT OF 1 LITER	BOILING POINT	NAME	WEIGHT OF 1 LITER	BOILING POINT
Acetylene . . .	1.1621	— 83.6°	Hydrogen chloride	1.6398	— 85.0°
Air . . . . .	1.2930		Hydrogen sulfide	1.5392	— 59.6°
Ammonia . . .	0.7708	— 33.3°	Methane . . . .	0.7168	— 161.4°
Argon . . . . .	1.7824	— 185.7°	Nitric oxide . .	1.3402	— 151.0°
Carbon dioxide .	1.9768	sublimes	Nitrogen . . . .	1.2506	— 195.8°
Carbon monoxide	1.2504	— 192.0°	Nitrous oxide . .	1.9777	— 89.5°
Chlorine . . . .	3.214	— 34.6°	Oxygen . . . . .	1.4290	— 183.0°
Helium . . . . .	0.1785	— 268.9°	Sulfur dioxide .	2.9266	— 10.0°
Hydrogen . . . .	0.08987	— 252.7°			

## ELECTROCHEMICAL SERIES

1. Cesium	8. Aluminum	15. Nickel	22. Antimony
2. Rubidium	9. Manganese	16. Tin	23. Mercury
3. Potassium	10. Zinc	17. Lead	24. Silver
4. Sodium	11. Chromium	18. Hydrogen	25. Palladium
5. Lithium	12. Cadmium	19. Copper	26. Platinum
6. Calcium	13. Iron	20. Arsenic	27. Gold
7. Magnesium	14. Cobalt	21. Bismuth	28. Osmium

TABLE OF THE CHEMICAL ELEMENTS, INCLUDING THEIR  
SYMBOLS, THEIR ATOMIC NUMBERS, AND THEIR ATOMIC  
WEIGHTS

NAME	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT	NAME	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT
Actinium . . .	Ac	89	—	Mercury . . .	Hg	80	200.61
Aluminum . . .	Al	13	26.97	Molybdenum . .	Mo	42	96.0
Antimony . . .	Sb	51	121.77	Neodymium . .	Nd	60	144.27
Argon . . . . .	A	18	39.94	Neon . . . . .	Ne	10	20.183
Arsenic . . . .	As	33	74.96	Nickel . . . . .	Ni	28	58.69
Barium . . . . .	Ba	56	137.36	Nitrogen . . . .	N	7	14.008
Beryllium . . .	Be	4	9.02	Osmium . . . . .	Os	76	190.8
Bismuth . . . .	Bi	83	209.00	Oxygen . . . . .	O	8	16.000
Boron . . . . .	B	5	10.82	Palladium . . . .	Pd	46	106.7
Bromine . . . .	Br	35	79.916	Phosphorus . . .	P	15	31.02
Cadmium . . . .	Cd	48	112.41	Platinum . . . .	Pt	78	195.23
Calcium . . . .	Ca	20	40.07	Polonium . . . .	Po	84	210.(?)
Carbon . . . . .	C	6	12.000	Potassium . . . .	K	19	39.10
Cerium . . . . .	Ce	58	140.13	Praseodymium . .	Pr	59	140.92
Cesium . . . . .	Cs	55	132.81	Protoactinium . .	Pa	91	—
Chlorine . . . .	Cl	17	35.457	Radium . . . . .	Ra	88	225.97
Chromium . . . .	Cr	24	52.01	Radon . . . . .	Rn	86	222.
Cobalt . . . . .	Co	27	58.94	Rhenium . . . . .	Re	75	188.7
Columbium . . .	Cb	41	93.1	Rhodium . . . . .	Rh	45	102.91
Copper . . . . .	Cu	29	63.57	Rubidium . . . .	Rb	37	85.44
Dysprosium . . .	Dy	66	162.46	Ruthenium . . . .	Ru	44	101.7
Erbium . . . . .	Er	68	167.64	Samarium . . . .	Sm	62	150.43
Europium . . . .	Eu	63	152.0	Scandium . . . .	Sc	21	45.10
Fluorine . . . .	F	9	19.00	Selenium . . . . .	Se	34	79.2
Gadolinium . . .	Gd	64	157.26	Silicon . . . . .	Si	14	28.06
Gallium . . . . .	Ga	31	69.72	Silver . . . . .	Ag	47	107.880
Germanium . . .	Ge	32	72.60	Sodium . . . . .	Na	11	22.997
Gold . . . . .	Au	79	197.2	Strontium . . . .	Sr	38	87.63
Hafnium . . . .	Hf	72	178.6	Sulfur . . . . .	S	16	32.06
Helium . . . . .	He	2	4.002	Tantalum . . . .	Ta	73	181.5
Holmium . . . .	Ho	67	163.5	Tellurium . . . .	Te	52	127.5
Hydrogen . . . .	H	1	1.008	Terbium . . . . .	Tb	65	159.2
Illinium . . . .	Il	61	—	Thallium . . . .	Tl	81	204.39
Indium . . . . .	In	49	114.8	Thorium . . . . .	Th	90	232.12
Iodine . . . . .	I	53	126.932	Thulium . . . . .	Tm	69	169.4
Iridium . . . . .	Ir	77	193.1	Tin . . . . .	Sn	50	118.70
Iron . . . . .	Fe	26	55.84	Titanium . . . .	Ti	22	47.90
Krypton . . . . .	Kr	36	82.9	Tungsten . . . .	W	74	184.0
Lanthanum . . .	La	57	138.90	Uranium . . . . .	U	92	238.14
Lead . . . . .	Pb	82	207.22	Vanadium . . . .	V	23	50.96
Lithium . . . .	Li	3	6.940	Xenon . . . . .	Xe	54	130.2
Lutecium . . . .	Lu	71	175.0	Ytterbium . . . .	Yb	70	173.6
Magnesium . . .	Mg	12	24.32	Yttrium . . . . .	Y	39	88.92
Manganese . . .	Mn	25	54.93	Zinc . . . . .	Zn	30	65.38
Masurium (?) . .	Ma	43	—	Zirconium . . . .	Zr	40	91.22

